A NEW COMPUTER REPRESENTATION OF THE PROPERTIES OF WATER SUBSTANCE

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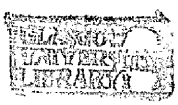

PREFACE

This thesis forms a record of the investigation carried out by the author on the correlation of the thermodynamic properties of ordinary water substance.

The background to this problem was thoroughly explored and is discussed together with details of the latest international developments.

Attention is drawn to the fact that the derivation of so-called 'Thermodynamic Temperatures' by the addition of the quantity, 273.15, to temperatures referred to the International Practical Temperature Scale leads to discrepancies in the values of the thermodynamic properties calculated from equations of state by means of the thermodynamic relations. These differences are shown to be significant when compared with the tolerances in the 1963 International Skeleton Tables.

Equations in the form of Chebyshev polynomials are presented which enable the thermodynamic properties of saturated water and steam to be calculated in a systematic manner. In the equation defining the pressure-temperature relationship allowance has been made for certain unpublished measurements of the National Bureau of Standards. Accurate tables of saturation properties for regular intervals of temperature are included.

A new equation for compressed water from 1 to 1000 bar and 0 to 150 ^{o}C in which the dependent variable is enthalpy and the independent variables are pressure and entropy is described. As these are the most important properties in pump and turbine performance, an example of the calculation of the efficiency of a water turbine using the 'thermodynamic method' described by Thom (99) is included.

Recommendations for future work are made and an outline of the advantages of an h-s-p formulation based on orthogonal Chebyshev polynomials is given. The work is concluded with an evaluation of the theoretical 'characteristic curves' for water.

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NOMENCLATURE

NOTATION

Subscripts

c,cl	critical point
f	saturated liquid
g	saturated vapour
s,σ	saturation
t	triple point

Reduced dimensionless quantities

$\delta = p/p_{cl}$	pressure
$\theta = T/T_{cl}$	temperature
$\chi = v/v_{cl}$	volume
$\zeta = h/p_{cl}v_{cl}$	enthalpy

Defined critical quantities

$p_{cl} = 22\ 120\ 000\ N/m^2$

$T_{cl} = 647.3\ K$

$v_{cl} = 0.00317\ m^3/kg$

SYMBOLS: The symbols used in the text (excepting Chapter 3) have the following meaning and units.

The constants used in the thesis are not listed as they are too numerous.

c_p	J/g K	Specific heat capacity at constant pressure
c_p^o	J/g K	Specific heat capacity at zero pressure
c_v	J/g K	Specific heat capacity at constant volume
c_σ	J/g K	Saturated specific heat capacity
f	J/g	Specific free energy (Helmholtz function)
g	J/g	Specific free enthalpy (Gibb's function)
g'	m/s^2	Acceleration due to gravity
h	J/g	Specific enthalpy
p	bar	Pressure
q	J/g	Heat per unit mass

R	J/g K	Specific ideal-gas constant
s	J/g K	Specific entropy
t	^{o}C	Temperature on the International Practical Celsius Scale
T	K	Thermodynamic temperature
$T_i(x)$		Chebyshev polynomial
u	J/g	Specific internal energy
v	cm^3/g	Specific volume
v_A	cm^3/g	Specific volume at one atmosphere (p_A)
V	m/s	Velocity
W	m/s	Velocity of sound
z	m	Height above datum
Z		Compressibility factor, pv/RT
α	J/g	Saturated liquid property defined by Osborne
α_p, α_σ	K^{-1}	Coefficient of thermal expansion
β		Reduced pressure
β'	J/g	Saturated liquid property defined by Osborne
β_s	cm^3/J	Adiabatic coefficient of bulk compressibility
β_T	cm^3/J	Isothermal coefficient of bulk compressibility
γ	J/g	Saturated vapour property defined by Osborne
γ_v, γ_σ	J/cm^3 K	Thermal pressure coefficient
θ		Reduced enthalpy
η_{tu}	%	Efficiency of turbine
τ	^{o}K	Temperature, $\tau\ ^{o}K = t^{o}C + 273.15$
Θ		Reduced temperature
X		Reduced volume

CHAPTER 1

HISTORICAL BIBLIOGRAPHY

1.1 Introduction

The early investigators of 2000 years ago were among the first to appreciate the unlimited applications of steam powered inventions. They had no knowledge of actual property values of water substance, but they were familiar with some of its practical aspects. The first recorded use of steam was by Hero of Alexandria, about 150 B.C., who described and illustrated 78 inventions. Amongst the number were a syphon, a pump, a water clock and a steam engine.

After this early use of steam there was a complete lapse in both interest and progress until the upsurge of science in the sixteenth century. This next period saw the development of the steam engine for various uses and in many varied forms, along with other types of steam operated apparatus, but it was not until the end of the eighteenth and the beginning of the nineteenth centuries that engineers realised that they were dealing with a non-ideal gas whose properties had to be determined experimentally, and not theoretically. From this realisation, there followed the study of steam properties which has continued unabated since this period and has continued to provide experimental values of increasing accuracy for the various properties.

The earliest known researches into the phenomena of steam, undertaken with a philosophical purpose, were those of Ziegler in 1769. Between this date and 1844 when Regnault (1) published the first of his memoirs, a large number of experiments were carried out by different workers who produced results of varying accuracy. However the first researcher to carry out accurate and consistent measurements was Regnault. He designed and built apparatus with which he was able to measure property values with an accuracy that was not surpassed for over fifty years. As a result he was able to develop equations and steam tables which accurately reflected his experimental

measurements. This was the pattern that was to emerge, as the investigation into the properties of water substance gathered momentum measurements would be made, then tables at rounded intervals of pressure or temperature would be compiled, and finally equations would be devised to represent the experimental or tabular values. This process has, of necessity, been continuous since more accurate measurements continue to be made.

The first equations were based on a combination of theoretical and graphical methods while modern formulations have either been based on theory and calculated by computer or been based solely on mathematical analysis of all available measurements.

In order to appreciate fully the latest progress in formulating equations to represent the thermodynamic properties of water substance, it is necessary to follow the various stages through which data representation has passed. For ease of description, this historical summary will discuss firstly the saturation equations and secondly the formulations which have represented water substance in its varying forms.

1.2 Saturation Line

A great variety of equations have been suggested to represent the different saturation properties. The most important one is the vapour pressure equation in which the pressure is normally represented as a function of temperature. This is due not only to the importance of the physical property itself but also to its relation to other thermodynamic properties, such as the latent heat of vaporisation. Various other properties have been measured also, the best known and most important of which are liquid volume, latent heat and specific heat. A detailed description of vapour pressure equations will be given but equations for the other properties will only be mentioned in passing.

1.2.1 Vapour pressure equations

The very earliest vapour pressure formula was given by Dalton (2) in 1801

who observed that the pressures increased in geometric progression while the temperature increased in arithmetic progression, that is

$$\log p = a + bT \qquad \ldots\ldots(1).$$

This relation was quickly disproved when better measurements became available. A completely different form was suggested about this time by De Prony (3)

$$p = aA^t + bB^t + cC^t + \text{——} \qquad \ldots\ldots(2)$$

and was followed by the relationship invented by Young (4) where

$$p = a(1 + bt)^m \qquad \ldots\ldots(3).$$

Equation (3) was used by many physicists over the next decade. In 1828 Professor Roche (5) suggested an equation of the form

$$p = ab^{t/(1 + ct)} \qquad \ldots\ldots(4).$$

Equation (4) can be generalised by making the temperature series into a double power series as follows;

$$p = ab^{\sum c_i t^i / \sum d_i t^i} \qquad \ldots\ldots(5).$$

This approach was tried by various people and culminated in the rather elaborate equation of this form devised by Broch (6) in 1881.

In his attempt to find a suitable relationship, Biot (7) (1844) modified equation (2) to

$$\log p = a + bB^t + cC^t \qquad \ldots\ldots(6).$$

Regnault (8) in 1847 formulated a modified version, (7), of equation (6) based on his experimental results, which provided the best representation to the data up to that time,

$$\log p = a + bB^x + cC^x \qquad \ldots\ldots(7)$$

where $x = t - d$,

None of the equations, up to this date, had any particular theoretical significance, as most of them were based on the graphical approach. However after this period many of the formulae were based on theoretical considerations,

the most common of which was the Clausius-Clapeyron relation

$$\frac{dp}{dt} = \frac{\Delta h}{T \Delta v} \quad .$$

In 1849, Rankine (9) produced one of the first equations, (8), to be derived from this theory

$$\log p = a - \frac{b}{T} - \frac{c}{T^2} \qquad \ldots\ldots(8),$$

and nine years later Kirchhoff (10) using the same background proposed

$$\log p = a - b \log T - \frac{c}{T} \qquad \ldots\ldots(9).$$

The last of the simple equations (10) was suggested by Antoine (11) in 1888, and originated from the algebraic equations for the hyperbola and the parabola.

$$\log p = a - \frac{b}{t + c} \qquad \ldots\ldots(10).$$

This type of equation did not find nearly as much support when it was first presented by Antoine as it has obtained in the period from 1945 up to the present.

Thiesen (12) produced a much more complicated equation in 1899 which he based on measurements which he had carried out himself. His equation can be simplified to

$$(t + a) \log p = b + ct + d(e - t)^4 \qquad \ldots\ldots(11).$$

In1907, Henning (13) carried out a survey of eleven equations which were in use at that time and compared them with Thiesen's equation. The following year Holborn & Henning (14) published accurate results and provided a correction curve to be used in conjunction with equation (11). Professor Callendar (15) published his steam tables in the 1920's and produced an equation, which was based very closely on the Clausius-Clapeyron relation,

$$\log p = a - \frac{b}{T} - c \log T + d \log \left(\frac{1 + z}{1 - z}\right) + e \frac{p}{T} \qquad \ldots\ldots(12),$$

where $z = \frac{kp}{T}$.

As can be easily appreciated it was necessary to interpolate in it for p

as both p and T appear in a rather complicated manner on the right hand side of the equation.

In the midst of these complicated forms there appeared in 1924, proposed by Henglein (16), a very simple equation

$$\log p = a - \frac{b}{T^n} \qquad .....(13)$$

to be followed in 1927 by one (14) by Batchinski (17) where temperature was the independent variable

$$t + a = b(\sqrt[4]{p} - 10^{c - d/\log(p_c/p)}) \qquad .....(14)$$

Three years later Hofbauer (18) produced a rather unusual equation

$$\log \log p = a + \log(T - b) - \log T - c \log \left(\frac{T}{d}\right) \qquad .....(15)$$

and in 1932, using natural logarithms, Kirčef (19) suggested

$$p - \ln p = a(T - b \ln T) + c \qquad .....(16).$$

All the equations so far mentioned had originated in Europe, particularly France, but the next two equations of note were both prepared in the U.S.A. The first, equation (17), was devised at Massachusetts Institute of Technology (MIT) by Smith, Keyes and Gerry (20) and was calculated by "least squares";

$$\log {}^{p_c}/_{p} = \frac{x}{T}\left(\frac{a + bx + cx^3 + ex^4}{1 + dx}\right) \qquad .....(17)$$

where $x = T_c - T$.

The second was devised, also in 1934, by Osborne & Meyers (21), who took a simple equation and added correction terms until they obtained an adequate fit to the data over the complete range. They obtained

$$\log p = a + \frac{b}{T} + \frac{cx}{T}(10^{dx^2} - 1) + e\,10^{Ay^{1.25}} \qquad .....(18)$$

where $x = T^2 - k$, $y = t_c - t$.

The final equation (18) was generally accepted and, with the addition of a more accurate equation (19) formulated by Gerry, and noted in reference (22), to cover the temperature range 0 °C to 100 °C, has been used internationally up until the last four years when many new empirical equations have been

devised using computers. Gerry obtained

$$\log p = a + b \log T + cT + \frac{d}{T} \qquad .....(19).$$

Dorsey (23) in 1940 reviewed the work done over the previous 20 years and concluded that equation (18), used over the temperature range - 5 °C to the critical temperature gave the best agreement to the experimental results.

Thomson (24) in 1946 advocated the use of the Antoine equation to represent the vapour pressure of any substance and showed that over a small range it would fit the data with great accuracy. This approach to the problem was repeated by the American Petroleum Institute (25) who, in 1964, represented the vapour pressure of water in the range 0 °C to 150 °C by nine Antoine equations, each covering a small range of temperature.

In the period 1963 - 66 polynomial series of the form (20) have been suggested by workers in Japan and Germany, viz

$$\ln p = \sum_i a_i x^i \qquad .....(20)$$

where $x = (1 - \theta)$ or $(T - T_o)$ or t.

With the advent of computers this type of equation is likely to find permanent recognition due to the ease with which it may be programmed.

1.2.2 Other saturation equations

Saturation properties other than vapour pressure have been measured and these include the total heat or enthalpy, latent heat, specific heat and liquid volume. The most important of these is the last mentioned and will be dealt with first.

The first liquid volume equation of any note, (21), was proposed by Tate & Fairbairn (26) in 1860.

$$v_s = a + \frac{b}{p + c} \qquad .....(21)$$

It was unusual in that it used pressure as the independent variable instead of temperature. The only other equation of any significance was devised by Smith & Keyes (27) in 1934 as part of a research project which was being undertaken at MIT. This equation, (22), has been formulated to give the

critical volume exactly and has been achieved by using $(t_c - t)$ as the independent variable.

$$v_s = \frac{v_c + ax^{1/3} + bx + ex^4}{1 + dx^{1/3} + ex} \qquad \ldots\ldots(22)$$

where $x = t_c - t$.

The other properties mentioned here have been represented by simple equations which have usually been in the form of a polynomial series.

There is, however, one research group who spent the years between 1930 and 1940 providing measurements and equations for the saturation properties. This work was carried out at the National Bureau of Standards using as their basis the calorimetric quantities α, β' and γ which are described by Osborne (28). From these quantities, which are fully described in Chapter 4, one can obtain all the saturation properties. This work has never been bettered and the equations and results obtained from it are still used in steam tables to-day. Unfortunately it is partly made up of equations and partly of tables and so is rather unwieldy to use. Hence the provision of straightforward equations based on this data would define the saturation properties in a much more satisfactory manner.

1.3 Equations of state

The representation of the properties of water substance has, much more so than the saturation properties, been attempted by both theoretical and empirical equations. In the theoretical approach, water substance in the vapour phase has been considered as an ideal gas and then modifications, based on theoretical considerations, have been made to the original relation to account for the differences between theoretical and experimental results. Partington and Shilling (29) have followed these developments by listing 56 equations of state. The empirical equations, on the other hand, appear to have been developed by the experimenters, who would formulate a simple

equation to reproduce their results and then produce steam tables from it. These two attitudes will be discussed separately.

Before continuing with the discussion in this chapter it is necessary to understand what is meant by the expression 'equation of state'. The definition has varied over the years and a slightly different form will be advanced here. The conventional definition may be expressed as follows:-

The properties of a fluid of constant chemical composition are completely defined when any two of three variables are known. These variables are p-v-T and any equation representing the interdependence of these three variables for a fluid is therefore an equation of state. Thus the general form of such an equation is

$$f(p, v, T) = 0.$$

The presently accepted definition agrees with the definition in general but not over the choice of variables. Here an equation of state or characteristic equation is taken to refer to an equation of three variables, for which, if any two are known then all the other thermodynamic properties may be calculated directly. Throughout the thesis the latter meaning will be used.

1.3.1 Theoretical equations

The first theoretical equation was suggested by Boyle and Lussac (30) in 1662 for an ideal gas and is written

$$pv = RT \qquad .....(23).$$

This form was used for almost 200 years until Rankine (31) in 1854 suggested a modified form, (24), which agreed more closely with the experimental results.

$$pv = RT - \frac{a}{Tv} \qquad .....(24).$$

After this improvement had been appreciated, a large number of varied forms were presented. The next important step forward was made by van der Waals (32) in 1873 who suggested equation (25) which has been used as a basis for more accurate equations by writing the constants a and b as functions of

volume and temperature

$$(p + \frac{a}{v^2})\ (v - b) = RT \qquad .....(25).$$

Another well known and popular form was devised by Dieterici (33) in 1898 where an exponential term was introduced

$$p(v - b) = RT\ \exp(-\frac{a}{RTv}) \qquad .....(26).$$

If the exponential in equation (26) is expanded as a power series and only the first term taken then equation (25) is obtained. Further improvements are represented by the equation (27) which Berthelot (34) put forward two years later

$$(p + \frac{a}{Tv^2})\ (v - b) = RT \qquad .....(27).$$

There were many other equations of a similar nature suggested but none of them managed to predict the experimental properties with any greater accuracy.

There was, however, one equation with which it was possible to obtain reasonable agreement with the experimental values. This was the 'virial equation' which could be written in two slightly different forms:

$$pv = A\ (1 + \frac{B}{v} + \frac{C}{v^2} + ...\ ) \qquad .....(28)$$

and

$$pv = A\ (1 + Bv + Cv^2 + ...\ ) \qquad .....(29)$$

where A, B, C, ... are called the first, second, third, ... virial coefficients and are functions of temperature. If only the first term is used in equations (28) or (29) then the ideal gas equation (23) is obtained. However this form of equation is usually used with the constants fitted as empirical functions of temperature.

In fact, all the equations that have been mentioned in this section are usually rewritten with their coefficients as functions of temperature, pressure or volume in order to give a much better approximation of the properties. A full description of this approach is discussed in Chapter 2 where the most recent advances in this field are considered and described.

1.3.2 Empirical equations

The equations mentioned at the end of the previous chapter were both theoretical and empirical in comparison with the entirely empirical equations which will now be described. Some of the ideal equations already discussed have been considered for use in the calculation of steam tables e.g. Callendar (35), but generally a simpler form of equation is chosen. The theoretical equations always use pressure, volume and temperature as the variables whereas with empirical equations almost any combination of variables are used.

The most common dependent variable, however, appears to be enthalpy. Regnault was the first person to produce a simple relationship to define enthalpy:

$$h = a + bt \qquad \text{.....(30).}$$

This equation (30) and the others which follow are applicable only for superheated steam. Marks and Davis (36) in compiling their steam tables modified equation (30) by adding an extra term to obtain

$$h = a + bt + ct^2 \qquad \text{.....(31).}$$

Holmes and Hollitch (37) provided three equations of the form

$$h = \sum_{i=0}^{4} \sum_{j=0}^{4} a_{ij}\, p^i (s - s_o)^j \qquad \text{.....(32)}$$

$$\text{where} \quad s_o = \sum_{i=0}^{5} b_i\, p^i$$

which they used for predicting steam turbine power plant performance. These equations gave good agreement with the enthalpy values from Keenan and Keyes' Steam Tables (38) but were not evaluated for the derivatives. The only other work using enthalpy as the dependent variable was carried out about the same time by Steltz and Silvestri (39) who produced equations for enthalpy, entropy and volume as functions of temperature and pressure. These equations were not in any way connected but were completely empirical. The method used

would appear to be based on finding a simple equation which provided an approximate fit to the data and then obtaining an accurate representation by the addition of correction terms.

The only other equations of any interest are two which were conceived in 1936 at MIT. The first of these was also for steam and is written

$$v = \frac{aT}{p} + B \qquad .....(33)$$

where $B = f(\frac{1}{T})$.

The second is a compressed water equation,

$$v = a + bx^c - dy^{e(p-a)} + \delta \qquad .....(34)$$

where $x = t_c - t$, $y = B - t$

and δ is a function of p and t which is treated graphically.

The only other approach to the problem of representing thermodynamic data by equations is to use an interpolation procedure along with the table values. This is a reasonable method only as long as a large amount of storage space is readily available on a computer, and for this reason it has not received much support.

CHAPTER 2

OUTLINE OF RECENT INTERNATIONAL DEVELOPMENTS

2.1 Introduction

As the properties of water substance are of such great importance to industry due to their use in boilers, pumps and other machines, a lot of interest and cooperation has taken place over the years on an international scale. The first international meeting, called the First International Conference on the Properties of Steam (1st ICPS), took place in London in 1929, and since then they have taken place at intervals over the intervening period. The last meeting, the Sixth, was held at New York in October 1963, and the results of this meeting (40) and the subsequent effects are now described, as they had a large bearing on the work described in this thesis.

2.2 The Sixth International Conference on the Properties of Steam

This conference first of all approved the new International Skeleton Tables (IST) prepared by the International Coordinating Committee of the 5th ICPS which had met in London in 1956. These Skeleton Tables, which are normally referred to as the 1963 IST, replaced the earlier 1934 IST which, in view of all the experimental work carried out since their inception no longer represented the state of knowledge of the properties. The 6th ICPS also discussed its own future and the present and future experimental work to be carried out, but the most important decision it made was in regard to formulations for computer use. An International Formulation Committee (IFC) was created to develop at the earliest practical date, within a year if possible, a formulation of the properties of steam, represented by the 1963 IST, for use with computers. The countries which composed this committee were Czechoslovakia, German Federal Republic, Japan, U.K., U.S.A. and U.S.S.R., since the bulk of the work on correlating equations and formulating steam tables had been and was being carried out by them.

These then were the decisions and recommendations of the 6th ICPS by whom the IFC was created and whose results will be discussed further on in this chapter. Now at this conference two very interesting and informative papers were given on the subject of formulations for computer use. A brief resumé of these papers and their salient points will now be given such that the advance of computer formulations and the slightly different approach of the various countries up to the present time can be discerned.

The first address on the subject 'Formulations for computer use' was given by Dr. K.R. Schmidt of the B.R.D., in which he suggested that this title had a triple sense, relating to the three purposes to which these formulations are directed, namely:-

(a) that of smoothing and correlating measured values

(b) that of making better Skeleton Tables or Steam Tables

(c) that of using these improved tables for technical and scientific computations.

In the past the desire for accurate knowledge of the properties of water led to the 1st ICPS in London in 1929 where it was decided to represent the accuracy of all experimental work by so-called Skeleton Tables with tolerances to give a measure of the probable accuracy. This process of forming new IST was continued over the years, the final IST (1963) being approved at the 6th ICPS.

Up until a few years ago all calculations were done by hand, now these calculations are being carried out on an ever-increasing scale by digital computers. However, this now raises the problem of efficient use of computer time. The storage of steam tables in the computer is not practical due to the large storage area required and the slow access time but even if the tables are reduced in size and interpolation formulae used these factors are still excessive.

The ideal position would be one with an internationally approved

formulation from which all steam tables, if required, would be calculated. The following conditions must be satisfied by any equations established for computer use:

(a) All values calculated from the equations must be within the tolerances of the IST.

(b) Maximum range of application, including the saturation line.

(c) Thermodynamic consistency, and differentiability over the whole range of application.

(d) Small storage space.

(e) Short computing times.

Since in the majority of cases the temperature T and pressure p are the given quantities the formulations should have the form:

$$v(p, T) \qquad h(p, T) \qquad s(p, T).$$

It would probably not be possible at this point of time to establish one unique function fulfilling all these requirements and so it would be necessary to accept several separate functions as applying in different regions e.g. compressed water, superheated steam and critical region. All equations so far proposed are valid only over limited regions such as these.

The second address on this subject was given by R.W. Bain of N.E.L., who had already formulated equations for water and steam using the form, pressure as a function of density and temperature. He thought there were three possible pairs of independent variables which could be used in a computer equation for use in power cycle calculations:

(a) pressure and temperature - This combination is the most popular although it does not appear possible to cover the entire range of the variables with a single equation.

(b) density (or volume) and temperature - This form is not quite so convenient but it seems to offer the best method of correlating the mass of experimental data.

(c) pressure and entropy - This equation would be just as convenient

as (a) and because of the continuity of all the thermodynamic functions across the two-phase region there is a strong possibility of being able to devise a single equation which will cover both the liquid and vapour regions. Unfortunately any equation of this form must use an equation of forms (a) or (b) to calculate initial enthalpies and entropies.

He then continued by giving his personal opinion on equations in general. There should not be any limit on the number of separate equations since if there was only one approved it would imply that there was no tolerance and this is definitely not the case. However these equations must satisfy some criteria. The obvious one is agreement with experimental knowledge and this could be modified to agreement with Skeleton Tables preferably with more entries. A necessary extension would then be to provide tables and tolerances of other properties e.g. specific heat, the Joule-Thomson coefficients and the derivatives of pressure.

In any calculations where there is uncertainty in the basic data an assessment of the uncertainty of the answers should be included and it is quite possible to do this simply on computers. This perhaps adds one further criterion, namely that a suitable equation should include in its description a statement of the errors in its coefficients and of how they are statistically correlated. With this addition more realistic answers to calculations could be obtained.

From these two addresses some of the differences in approach are obvious, mainly due to the fact that Schmidt is an industrialist and that Bain is a scientist. Their attitude also reflects the views of their own countries which will become more obvious later in this resumé.

Meanwhile in the U.K. the work of computer formulation has been carried

out on both a national and an international level and they will be described in conjunction.

After the Sixth ICPS work in Britain was carried out in three main centres - Cambridge University, N.E.L. and Glasgow University - and discussed and coordinated in the Computation Panel of the Electrical Research Association (ERA) Committee 2B.* Most of the work prior to this had been carried out at NEL by Bain and Le Fevre who together carried out a theoretical survey (41) of possible forms of equation some of which were mentioned by Bain in his address to the Sixth Conference. These suggestions were examined at Cambridge by Haywood and Bott (42) and they divided the problem up into stages as follows:

(a) Plots of various forms of h - s - p.

(b) Examination of methods of curve and surface-fitting.

(c) The results of curve fitting both the saturation line and a few chosen isobars for h = h(s). Unfortunately they were not able to carry their investigation any further but the conclusions that they reached provided a sound basis for any future work.

Meanwhile at NEL, Bain had left, and the work was being carried on by R.I. McLeod who carried out a short review (43) of this earlier work and continued by writing a surface fitting program to fit a surface for s = s(h, ln p).

During this period the work described in this thesis was initiated at Glasgow. This consisted of first providing an equation for the saturation line of the form s = s(ln p) which could be used with McLeod's surface and following that a vapour pressure equation.

2.3 International Formulation Committee

The First Meeting of the IFC was held in Prague in March 1965 at which the results of the above mentioned research was reported (44).

*Now U.K. Committee on the Properties of Steam - Ministry of Technology.

However before approving of any computer formulation it was found necessary to define explicitly the problem facing the IFC. This was done in Resolution 2 which may be summarised as follows:

There would appear to be two objects:

Object A: The determination, correlation, tabulation and formulation of the actual properties of natural water substance. (Actual properties are, of course, never exactly known and statements about them must be given limits of error.)

Object B: The definition, by stating its properties, of a conceptual fluid, 'contractual steam'. (A definition, by its nature is exact.)

Object A would be met by sharing, among National Delegations, the work on the following four sub-regions:

(a) superheated vapour

(b) critical

(c) compressed liquid

(d) saturation line.

From the results of this work a formulation should be agreed and adopted and a formula for tolerances prepared for use with the formulation.

Object B, while being partly satisfied by the above may only be fully satisfied by the preparation of transformed formulations.

It was suggested that the tasks (a), (b), (c), and (d) be divided thus:

(a) USSR

(b) CSSR

(c) BRD

(d) UK.

Following on from the definition of the problem it was felt necessary to provide criteria which any equations must satisfy if they were to gain recognition by the IFC. These criteria may be enumerated as follows:

(1) The entire field of the 1963 IST must be covered.

(2) The specific internal energy and the specific entropy must be zero at the triple point.

(3) As density → 0 then $^{pv}/_{T} \rightarrow R$ where R = (461.51 ± 0.07) J/kg ^{o}K.

(4) Thermodynamic consistency must be maintained.

(5) Discontinuities on inter-regional boundaries should be less than the recommended maximum acceptable discontinuity.

(6) Isothermal (or isobaric) changes across the saturation line should be less than the maximum recommended value.

(7) Suitability for use in industrial calculations and simplicity.

(8) Cumulative computational rounding errors should not exceed $10^{-(x-2)}.y$ where x is the number of significant figures that can be held in the computer and y is the property being calculated.

(9) The combined virtues of minimum arithmetic operations and minimum computer storage.

The IFC adopted for its work the symbols and units to be used as well as a dimensionless form of the properties for use in the equations.

Two formulations had been presented to the meeting for consideration. The first, correlated by Dr Juza (45) of the CSSR, is of the form p = p(v,T) which is not very suitable for industrial calculations due to the form of variables and its complexity, although it is very accurate. The other was presented by the BRD delegation and did not have the drawbacks of the above-mentioned although its inter-regional discontinuities were somewhat large. It was proposed by Professor Le Fevre, the leader of the U.K. delegation, that this formulation should be given temporary recognition once it had had some improvements, which he suggested, made to it. These modifications are:

(1) the formulation shall be in the form agreed at the Prague meeting of the IFC

(2) the formulation shall include an expression for the saturation lines

(3) the inter-regional boundary between the superheated vapour and the critical region shall be unambiguously stated.

It was resolved that the above task would be entrusted jointly to the BRD

and UK delegations.

After the First IFC meeting the research continued at both NEL and Glasgow University until just before the Second IFC meeting, which was held in Glasgow in March 1966, when a vapour pressure equation had been formulated as part of the UK contribution to Object A.

McLeod had completed his first attempt to provide a formulation of the type $s = s(p, h)$ and he submitted a report (43) to the Computation Panel on his conclusions. He decided that there was no possible simple representation available in the above form but he suggested that $h = h(s, p)$ might give better results and that if the fit was constrained along the saturation line and the derivatives ignored, at least, initially, more success might be obtained. Meanwhile at Glasgow the other saturation equations were being completed prior to tackling the surface fitting problem.

At the Second Meeting (46) equations for the sub-regions were presented and in order to fulfil Object A two Formulation Working Groups were set up. The first, composed of the BRD, CSSR and USSR were to construct the formulation and to prepare a technical report and the second, composed of Japan, UK and USA, were to check the formulation independently.

As a fulfilment of Object B the formulation prepared by the UK and BRD was awarded temporary recognition and the equations were published (47) in March 1966.

It had been discovered that the Japanese had obtained a critical equation which if inserted in the approved formulation would considerably improve it and it was decided to invite collaboration over providing this improvement. This resulted in the improved 1967 formulation (48) which was given temporary recognition in place of the 1966 formulation.

The third and final IFC meeting (49) was held in Paris in April 1968 to consider the formulation which had been prepared as part of Object A. This formulation composed of the four sub-regions indicated at Prague, and called 'First IFC Master Formulation', had been checked and after some small

modifications which included a change of title, was approved by the IFC.

However before disbanding the IFC passed a resolution in which it withdrew the designation 'temporary' previously qualifying its recognition of the 1967 IFC Formulation for Industrial use and submitted the following two Formulations to the 7th ICPS which was due to meet in Tokyo in September 1968.

(a) The 1968 IFC Formulation for Scientific and General Use, as providing the best current representation of the thermodynamic properties of steam.

(b) The 1967 IFC Formulation for Industrial Use, as providing equations better suited for use in industrial calculations.

It also recommended that despite the adoption of these two formulations, work should continue on formulations and on the production and international exchange of experimental data.

CHAPTER 3

CURVE AND SURFACE FITTING

3.1 Introduction

This chapter contains a discussion of both general and particular methods of curve and surface fitting. The mathematical details of the methods used are described so that the problem, which appeared in the course of the work, may be more fully appreciated. It is necessary also to include the numerical procedures involved in the use of Chebyshev series and the statistical criterion which help to find the 'best approximation' to the input data.

3.2 Curve fitting

Before the problem in hand could be tackled it was necessary to consider the possible methods of curve fitting which could be used. The only requirement was the ability to find a smooth equation to provide a close fit to the data, which would probably be available at unequally spaced intervals.

As was mentioned in Chapter 2, Haywood and Bott (42), at the suggestion of the Computation Panel of the E.R.A. Steam Committee 2B, carried out some preliminary fits for the saturation line using orthogonal Chebyshev polynomials. However, as this method, which is described in section 3.5.4, could only be used for the equally spaced problem, it was felt advisable to review the different methods that were applicable for unequally spaced data, even although there is a method of calculating the Chebyshev coefficients for the latter case.

3.2.1 Comparison of curve fitting methods

In 1964, Berztiss (50) carried out a detailed review of five different methods of curve fitting, which he labelled as follows:

A: power series;

B: series of Legendre polynomials;

C: series of Chebyshev polynomials;

D: series of orthogonal polynomials, generated by recurrence (Forsythe (51));

E: method D, modified to use Chebyshev polynomials (Clenshaw (52)).

Clenshaw and Hayes (53) in a paper entitled 'Curve and Surface Fitting' discussed these methods also, but drew slightly different conclusions. It is proposed, in addition to these methods, to discuss two other methods:

F: Antoine equations;

G: splines.

In the following, the methods will be referred to by their labels.

Methods A, B and C involve the direct solution of the respective normal equations in a straightforward manner. Method A is the simplest and most common curve fitting method and is often casually referred to as the method of 'least squares'. Unfortunately the normal equations which result are often very ill-conditioned and this limits A to low degree polynomials. Moreover, for each degree of polynomial fitted, an essentially different computation is involved. Hence A, although very useful for fitting a small amount of data to a low power, need not be considered further.

The recommendations, which Berztiss made, were based on the accuracy, storage requirements and amount of computation necessary for each method and he concluded by assessing their merit in certain specific situations. The severe disadvantages of method A have already been mentioned. The remaining four methods give results of comparable accuracy. E and B are the two slowest methods and as B has no compensating advantage it need not be considered. This leaves C, D and E. One factor which Berztiss did not take into consideration was, that for methods D and E, no prior knowledge of the degree is required and this provides a very definite

advantage. On account of this omission, Berztiss concluded that for the general case methods C and D were likely to be the best. However, because of this disadvantage method C will be discarded and this now leaves the choice between D and E on two opposing factors: E presents a convenient output in concise form while D, although it requires more storage, is considerably faster. As one of the most important considerations in curve fitting is the absolute necessity of being provided with enough information about every fit, in order to be able to make a reasoned choice between two possible equations, it seems more than reasonable to choose E as being the best method of the five.

Method F has been included in this discussion since Antoine equations have been used in the past to represent thermodynamic properties very successfully. The main advantage of F is its simplicity coupled with the fact that over a small range it can give a good representation of the data. It can also be extrapolated with no great loss of accuracy as it contains no high powers. It has the added advantage that due to its simplicity it can be worked out quickly by hand. Thomson (24) provides a good description of Antoine equations and their use in vapour pressure equations. However, there are two drawbacks; the first is the number of equations needed to cover the range of the data. A good example of this are the equations, which have been provided for the vapour pressure of water by the American Petroleum Institute (25). In order to obtain an adequate fit for the range of temperature 0 ^{o}C to 150 ^{o}C, nine different equations (27 constants) are required. The second drawback is the difficulty in deciding on how large a range one equation should cover.

Method G was not considered initially as a possible method, but it was felt, that due to the possibilities it presents, a brief description of it should be included. This method is basically rather similar to F although it is much more sophisticated. This subject is as yet only in its infancy and there is a lot of research being carried out at present

on it. Two of the leading workers in the field in this country are Curtis and Powell of the Atomic Energy Research Establishment. In September 1967, Powell gave a paper at the Conference organised by the Institute of Mathematics and its Applications on 'Numerical Approximations to Functions and Data' entitled 'Curve fitting by splines in one variable'. The particular function chosen was a cubic spline since it has the ability to adapt to a wide variety of curve shapes. An algorithm was supplied which requires the user to specify only his measurements with weights, and the remaining decisions are automatic. The basis of the algorithm is that the linear parameters of the spline are calculated to minimise the weighted sum of squares of residuals plus a smoothing term and the knots (joins in the adjacent equations) of the spline are determined by an iterative procedure. Initially only a few knots are chosen, but more are inserted if a statistical test suggests that the residuals have some significance, until no more trends are predicted. The smoothing term is needed to prevent the approximation from following data errors.

This method seems to be ideal for fitting curves with very pronounced waves or curves where it would be impossible to obtain an adequate fit using only one equation of any form. Method G also appears likely to suffer from the defect that a large number of coefficients may be necessary to represent the data.

The final and decisive reason for choosing method E is that it can be used for surface fitting problems as its output and ease of use make it particularly advantageous and that it had already been used successfully by Haywood and Bott.

3.2.2 Description of Forsythe's method modified by Clenshaw

This method is reproduced from the papers of Clenshaw (52) and Clenshaw and Hayes (53) as this chapter would not be complete without its description.

3.2.3 Forsythe's method

We first assume that the independent variable x has been normalised so

that its data values lie between -1 and +1; that is, if the data values of the original variable X, say, lie in the range $A \leq X \leq B$, then

$$x = (2X - A - B)/(B - A) \qquad .....(35).$$

The normalised variable is often modified to $x = (2X - C)/D$ in order to simplify the equation.

Let y_r ($r = 1, 2, \ldots, m$) be the observed values of a dependent variable y at the given values x_r. Then the polynomial $Y_k(x)$ of degree k which minimises the residual sum of squares

$$\delta_k^2 = \sum_{r=1}^{m} \{Y_k(x_r) - y_r\}^2 \qquad .....(36)$$

may be obtained by truncating the series

$$c_o\, p_o(x) + c_1\, p_1(x) + c_2\, p_2(x) + \ldots\ldots \qquad .....(37)$$

after the term $c_k\, p_k(x)$. The polynomial $p_i(x)$, of degree i, satisfies the orthogonality condition

$$\sum_r p_i(x_r)\, p_j(x_r) = 0 \ , \ i \neq j \qquad .....(38)$$

so that the coefficients c_i of the series (37) are given by

$$c_i = \sum_r y_r\, p_i(x_r) / \sum_r p_i^2(x_r) \qquad .....(39).$$

The polynomials $p_i(x)$ then satisfy the following three-term recurrence relation

$$p_{i+1}(x) = 2(x - \alpha_{i+1})\, p_i(x) - \beta_i\, p_{i-1}(x) \qquad .....(40)$$

where

$$\alpha_{i+1} = \frac{\sum_r x_r\, p_i^2(x_r)}{\sum_r p_i^2(x_r)} \ , \qquad \beta_i = \frac{\sum_r p_i^2(x_r)}{\sum_r p_{i-1}^2(x_r)} \qquad .....(41).$$

The recurrence process may be started by taking $\beta_o = 0$ and $p_o = 1$.

The polynomials $p_i(x)$ and $Y_i(x)$ are represented within the computer by their values at the points x_r. This method is described by Forsythe (51), and, with examples, by Ascher and Forsythe (54).

3.2.4 Clenshaw's modified method

Essentially the modification consists of a more compact storage procedure.

An obvious way to achieve economy of storage is to store the coefficients in their Chebyshev expansions given by

$$p_i(x) = \sum_{u=0}^{i}{}' p_u^{(i)} T_u(x) \qquad \ldots\ldots(42)$$

and

$$Y_i(x) = \sum_{u=0}^{i}{}' A_u^{(i)} T_u(x) \qquad \ldots\ldots(43)$$

where Σ' indicates a sum whose first term is halved and $T_u(x)$ is the Chebyshev polynomial in x of degree u. A description of Chebyshev polynomials is given in section 3.5.

The coefficients are generated by use of the relations

$$p_u^{(i+1)} = p_{u+1}^{(i)} + p_{|u-1|}^{(i)} - 2\alpha_{i+1} p_u^{(i)} - \beta_i p_u^{(i-1)} \qquad \ldots\ldots(44)$$

and

$$A_u^{(i)} = A_u^{(i-1)} + c_i p_u^{(i)} \qquad \ldots\ldots(45).$$

Equation (44) is obtained by substituting the series (42) in the recurrence relation (40) and must be initiated using $p_i^{(i)} = 1$ for $i \geq 0$, while equation (45) is derived on substituting the series (42) and (43) into the equation

$$Y_i(x) = Y_{i-1}(x) + c_i p_i(x) \qquad \ldots\ldots(46).$$

In this method the output will include the coefficients $A_u^{(i)}$ accompanied by all the required auxiliary quantities. These will be discussed in section 3.4 as they are closely related to the choice of 'best fit'.

An Algol program was written to carry out this method of curve fitting and a flow chart and print out of the program are included in Appendix III.

3.2.5 Weights

Sometimes it is necessary to obtain a weighted fit to the given data: that is; we need to find the polynomial $Y_k(x)$ of degree k which minimises the weighted sum of squares of the residuals

$$\delta_k^2 = \sum_{r=0}^{m} w^2(x_r) \{Y_k(x_r) - y_r\}^2 \qquad \ldots\ldots(47)$$

where the weights $w^2(x_r)$ are defined for each given point x_r. It is immediately obvious that the case already considered was in fact the particular one where $w^2(x_r)$ is constant for all values of x_r.

Thus to produce a weighted fit it is only necessary to introduce the factor $w^2(x_r)$ into equations (39) and (41) as follows

$$c_i = \sum_r w^2(x_r)\ y_r p_i(x_r) / \sum_r w^2(x_r)\ p_i^2(x_r) \qquad .....(48)$$

and

$$\alpha_{i+1} = \frac{\sum_r w^2(x_r) x_r\ p_i^2(x_r)}{\sum_r w^2(x_r)\ p_i^2(x_r)}, \quad \beta = \frac{\sum_r w^2(x_r)\ p_i^2(x_r)}{\sum_r w^2(x_r)\ p_{i-1}^2(x_r)} \qquad .....(49).$$

3.2.6 Constraints

It is a common phenomenon when fitting data, to require the curve to pass through a particular point, which may or may not be the origin, or for the curve to have an asymptote or vertical tangent. The first case could be equated to providing an infinitely large weight at the point and could possibly be tackled in this manner. However it is much more satisfactory and also simpler to constrain the curve, such that it satisfies the criterion. Method E can easily be modified to allow a general form of constraint to be used. A brief description now follows and is concluded with a simple example.

The fitting function y(x) may be written in the form

$$y(x) = \mu(x) + \nu(x)\ g(x) \qquad .....(50).$$

The functions $\mu(x)$ and $\nu(x)$ are defined by the constraints and g(x) is a polynomial. The quantity $\mu(x)$ is chosen to be a simple function satisfying the given conditions, while $\nu(x)$ is usually a polynomial which forces y(x) and its derivatives to adopt the same value as $\mu(x)$ and its derivatives wherever they are specified. For example the two conditions $y(x) = a$ at $x = 1$ and $y(x) = 0$ at $x = 0$ would be satisfied by taking $\mu(x) = ax^2$ and

$\nu(x) = (x - 1)x^2$.

The main restriction on using constraints in equation (50) is that the derivative of order q at any point can be forced by prescribing $\mu(x)$ and $\nu(x)$ only if $y(x)$ and its previous $(q - 1)$ derivatives are also forced at the same point. When these derivatives of lower order are not given, then they may be estimated and their estimates refined by an iterative procedure.

Instead equation (50) is modified as follows

$$y(x) - \mu(x) = G(x) \qquad .....(51).$$

The constraints are thus introduced by fitting $y_r - \mu(x_r)$ directly taking $p_o = \nu(x)$. Application of equation (40) ensures that $\nu(x)$ will therefore be a factor of $p_i(x)$ for all the values of i. As a result the function now being minimised is

$$\delta_k^2 = \sum_r \{G_k(x_r) - [y_r - \mu(x_r)]\}^2 \qquad .....(52)$$

where

$$G_k(x) = \nu(x)\, g_k(x) \qquad .....(53).$$

Hence the function $Y_k(x)$ is obtained from

$$Y_k(x) = \mu(x) + G_k(x) \qquad .....(54).$$

It can be seen that since $p_i(x)$ is an orthogonal polynomial that $\nu(x)$ must be an orthogonal polynomial also. If $\nu(x)$ is a polynomial of degree j then $p_i(x)$ will obviously be of degree $(i + j)$. The fact that $\nu(x)$ must be limited to polynomials only does not restrict the program unduly as most common requirements can be set up quite easily using appropriate forms of $\nu(x)$ and $\mu(x)$.

As an example: $y'(x) = y(x) = 0$ when $x = 1$ could give $\nu(x) = (x - 1)^2$. This means that $p_o(x)$ would take the following value, expressed in Chebyshev polynomials,

$$p_o(x) = (x - 1)^2 = \tfrac{1}{2}|T_2(x) - 4T_1(x) + 3|$$

Thus, where one equation would not suffice, two equations can be used as long as it is ensured that the function values and derivatives of both

equations at the join provide a smooth fit.

3.2.7 Derivatives

As the equations, which are to be formulated in the course of this research, require their first derivative to be fitted as accurately as the dependent variable, it was thought that this information could be used to increase the accuracy of the fit. A modification to Method E which will include derivatives in the fitting procedure will now be described.

Consider a set of m points where the values x_r, y_r and y'_r are known. Then, using the usual notation, it is necessary to minimise

$$\delta_k^2 = \sum_{r=1}^{m} \{Y_k(x_r) - y_r\}^2 + \lambda \sum_{r=1}^{m} \{Y'_k(x_r) - y'_r\}^2 \qquad .....(55)$$

where λ is the weighting coefficient.

The derivative Y'_k is calculated by differentiating equation (46) to give

$$Y'_k = Y'_{k-1} + c_k\, p'_k(x) \qquad .....(56)$$

where $p'_k(x)$ is similarly obtained from equation (40) such that

$$p'_{k+1}(x) = 2p_k(x) + 2(x - \alpha_{k+1})\, p'_k(x) - \beta_k\, p'_{k-1}(x) \qquad .....(57).$$

This recursion is initiated using $p_o = 1$, $\beta_o = 0$ and $p'_o = 0$.

In order to make the next part easier to follow, it will be expressed using matrix notation, with $k = 1$ and with $p_1 = p_1(x)$.

Equation (39) of method E may therefore be written in this form

$$\begin{bmatrix} \Sigma\, p_0^2 & \Sigma p_0\, p_1 \\ \Sigma\, p_1\, p_0 & \Sigma p_1^2 \end{bmatrix} \begin{bmatrix} c_0 \\ c_1 \end{bmatrix} = \begin{bmatrix} \Sigma\, y_0\, p_0 \\ \Sigma\, y_1\, p_1 \end{bmatrix} \qquad .....(58).$$

Now due to the orthogonality relationship (38), all the non-diagonal terms of the matrix are zero and this allows equation (58) to be simply solved.

However this is not the case when the derivatives are introduced as may be seen from equation (59).

$$\begin{bmatrix} \Sigma p_0^2 + \lambda \Sigma p_0'^2 & \Sigma p_0 p_1 + \lambda \Sigma p_0' p_1' \\ \Sigma p_1 p_0 + \lambda \Sigma p_1' p_0' & \Sigma p_1^2 + \lambda \Sigma p_1'^2 \end{bmatrix} \begin{bmatrix} c_0 \\ c_1 \end{bmatrix} = \begin{bmatrix} \Sigma y_0 p_0 + \lambda \Sigma y_0' p_0' \\ \Sigma y_1 p_1 + \lambda \Sigma y_1' p_1' \end{bmatrix} \quad (59)$$

Unfortunately, as the polynomial p_i' does not satisfy the orthogonality relation the non-diagonal terms will not be zero although they will probably be quite small. Hence it is necessary to solve this set of normal equations for the c_i. This must, of course, reduce the accuracy of the calculation by an unspecified amount. By varying the size of λ, however, it is possible to ensure that the off diagonal terms do not become too large, thus decreasing the accuracy of the solution.

3.3 Surface fitting

The problem of surface fitting (or data fitting in two independent variables) can be divided into three possible groups. Firstly there is the particular case where all the data presented is at the points of intersection of a rectangular mesh whose lines are parallel to the sides of a rectangular boundary (fig 1a). This will be called, following Clenshaw and Hayes (53) notation, problem (i). This problem has been dealt with by Cadwell (55) and De Lury (56) and is solved by repeated application of the curve fitting routine. Problem (ii) is slightly more difficult to deal with as the data points are scattered arbitrarily along lines which lie parallel to, say, the x-axis. The boundaries for this case are, as can be seen from fig 1b, two straight parallel lines and two curves. This problem occurs quite frequently in physical experiments and of course in ship-fairing. As in problem (i) we are able to solve problem (ii) by repeated application of curve fitting techniques. The completely general case, problem (iii), is represented by the one where the data is scattered in an arbitrary manner within a closed finite area, fig 1c. This method requires a complicated solution in terms of orthogonal polynomials in two variables and has been

demonstrated by Bain (67) and Cadwell and Williams (58).

As problem (ii) is the case considered here a description of it will now be given. In order to simplify the surface fitting procedure, especially if constraints are required, it was decided to reorganise the data to conform to a rectangular boundary. When constraints are applied the general case will be considered in theory although in practice it is avoided.

3.3.1 Adaptation of curve fitting method

It may be assumed, without loss of generality, that the data lie on lines of constant y i.e. $y = y_s$ $(s = 1, 2, \ldots, n)$. The x and z values of the points, as they lie in different positions on each y_s are denoted by $x_{r,s}$ and $z_{r,s}$ $(r = 1, 2, \ldots, m_s)$.

The curve fitting method E, which was described in section 3.2.4, may now be applied first of all fitting the curves for z in the x direction for each value of s.

$$z = \sum_{u=0}^{k}{}' a_{u,s}\, T_u(x) \qquad (s = 1, 2, \ldots n) \qquad \ldots\ldots(60)$$

and then fitting Chebyshev polynomials in y to the coefficients so obtained

$$a_u = \sum_{\nu=0}^{l}{}' b_{u,\nu}\, T_\nu(y) \qquad (u = 0, 1, \ldots k) \qquad \ldots\ldots(61).$$

Equations (61) and (62) may then be rewritten as

$$z = \sum_{u=0}^{k}{}' \sum_{\nu=0}^{l}{}' b_{u,\nu}\, T_u(x)\, T_\nu(y) \qquad \ldots\ldots(62).$$

3.3.2 Weights

If it is necessary to apply weights to any $z_{r,s}$ then it must be done when fitting equation (60). This would then require the application of the weighting technique as described in section 3.2.5 to equation (60) only, and not to equation (61).

3.3.3 Constraints

As in the curve fitting problem, it is often necessary to constrain the

fit such that two separate surfaces may have a smooth join at the common boundary. Normally the constraints are applied along the boundary curves $X = A(y)$ and $X = B(y)$. The variable X are then transformed by

$$x = \frac{2X - A(y) - B(y)}{B(y) - A(y)} \qquad .....(63).$$

Then the fitting function is of the form

$$z(x,y) = \mu(x,y) + \nu(x)\ g(x,y) \qquad .....(64)$$

where $\mu(x,y)$ is a simple function, not necessarily a polynomial, satisfying the constraints and $\nu(x)$ is a polynomial which ensures that $z(x,y)$ has the same behaviour as $\mu(x,y)$ wherever this is specified. It can now be written

$$Z(x,y) = z(x,y) - \mu(x,y) \qquad .....(65)$$

and this reduces the problem to

$$Z(x,y) = \nu(x)\ g(x,y) \qquad .....(66).$$

Equation (66) is analgous to equation (53) and is dealt with by setting $p_o = \nu(x)$ in equation (60).

In order to demonstrate the simplicity of using this method an example is now given. Take, for example, the conditions $z = \phi(y)$ and $\frac{\partial z}{\partial X} = \psi(y)$ along the boundary $X = A(y)$. The latter condition may be rewritten

$$\frac{\partial z}{\partial x} = \tfrac{1}{2}(B(y) - A(y))\ \psi(y)\ .$$

Thus the following equations for μ and ν would prove suitable

$$\mu(x,y) = \phi(y) + \tfrac{1}{2}(1 + x)\ [B(y) - A(y)]\ \psi(y)$$

and

$$\nu(x) = (1 + x)^2\ .$$

It can thus be appreciated that the constrained surface fitting problem is dealt with in an exactly similar manner to the curve fitting problem only with the addition of an extra dimension.

3.4 Criterion for goodness of fit

From the results obtained by using method E, it is necessary to decide

on the 'best fit'. The polynomial of best fit may be conceived as that which most effectively compromises between smoothness, as represented by the degree of polynomial, and closeness to the data, measured by the standard deviation. There are various different factors which can all be used in determining the best fit and which may also show up errors in the input data.

The first factor is the coefficients. If the data points being dealt with were exact values of a well-behaved mathematical function, the coefficients would decrease as the power i increased. In practice, however, the readings y_r invariably contain rounding and observational errors, which affect the behaviour of the coefficients. For values of i exceeding a certain value k, say, the coefficients will fluctuate about zero in an apparently random manner. The polynomial $Y_k(x)$ may then be accepted as the desired solution. Although it may sometimes be difficult to pick a definite value for k, the choice is not critical, since the difference in $Y_{k-1}(x)$, $Y_k(x)$ and $Y_{k+1}(x)$ for any value of x should be small.

The second factor is the statistical one; the standard deviation. The best value of i is that at which the standard deviation ceases to decrease significantly. This criterion is easy to apply although it is necessary to take care when applying it as the standard deviation may remain steady for two or three powers before decreasing again.

The third and final factor is the behaviour of the successive sets of residuals $Y_k(x_r) - y_r$. Examination of the complete set for each power would involve a lot of unnecessary work and so only the extreme values are inspected. Like the standard deviation, the numerically larger of P_i(largest positive residual) and N_i(largest negative residual) will decrease appreciably as i increases until k is reached.

However, the quantities P_i and N_i have another useful purpose. If one reading y_r has an outstanding error in it, then there will be a tendency for P_i or N_i to occur at the corresponding value of x_r for the different values of i.

Based on the information provided by these three criteria, the best fit

may be ascertained and large errors in the input data can be quickly spotted.

3.5 Chebyshev series

Before considering the series it is necessary to define the Chebyshev polynomial. This polynomial is represented by the notation $T_r(x)$ which is the Chebyshev polynomial of degree r in x defined by

$$T_r(x) = \cos(r \cos^{-1} x) \qquad .....(67)$$

where $1 \leq x \leq 1$.

It is possible to represent an arbitrary function f(x) by an infinite Chebyshev series

$$f(x) = \tfrac{1}{2}a_0 + a_1 T_1(x) + a_2 T_2(x) + ... \qquad (68)$$

which may be rewritten

$$f(x) = {\sum_{r}}' {}_0^{\infty} a_r T_r(x) \qquad .....(69)$$

where the prime indicates that the first term is to be halved. Then provided that the series converges reasonably rapidly, the function may be represented very closely by a finite series of order n.

$$f(x) = {\sum_{r}}' {}_0^{n} a_r T_r(x) \qquad .....(70).$$

Chebyshev polynomials are easily evaluated using the recurrence relation

$$T_{r+1}(x) = 2x T_r(x) - T_{r-1}(x) \qquad .....(71)$$

where the first two polynomials are defined by

$$T_0(x) = 1 \text{ and } T_1(x) = x.$$

Hence using equation (71) $T_2(x) = 2x^2 - 1$; $T_3(x) = 4x^3 - 3x$; etc.

3.5.1 Summation

It is possible to evaluate a Chebyshev series, with given numerical constants, for an arbitrary value of x, by evaluating all the Chebyshev polynomials and then summing the series. However, there is a faster and

more compact method which involves the use of the recurrence relation (72). The values $b_n, b_{n-1}, \ldots\ldots, b_o$ are calculated, in turn, from

$$b_r = 2x\, b_{r+1} - b_{r+2} + a_r,$$

$$\text{and } b_{n+1} = b_{n+2} = 0 \qquad \ldots\ldots(72).$$

Then

$$f(x) = \tfrac{1}{2}(b_o - b_2) \qquad \ldots\ldots(73).$$

3.5.2 Integration

Here it is necessary to obtain $\int f(x)\, dx$ where $f(x)$ is expressed as a Chebyshev series as in equation (70).

Thus it is possible to write

$$\int f(x)\, dx = \sum_{r=0}^{n+1}{}' A_r\, T_r(x) \qquad \ldots\ldots(74)$$

where

$$A_r = \frac{a_{r-1} - a_{r+1}}{2r} \quad (r > 0),$$

$$a_{n+1} = a_{n+2} = 0 \qquad \ldots\ldots(75)$$

and A_o is determined by the lower limit of integration. As the factor 2r is the divisor there is no loss of accuracy.

3.5.3 Differentiation

The method here is the exact opposite of that for integration. Given the Chebyshev series

$$f(x) = \sum_{r=0}^{n}{}' A_r\, T_r(x)$$

The coefficients, a_r, in

$$f'(x) = \sum_{r=0}^{n-1}{}' a_r\, T_r(x)$$

are calculated using the relation (75) in reverse as

$$a_{r-1} = a_{r+1} + 2r\,A_r \,,$$

$$\text{and } a_n = a_{n+1} = 0 \qquad \text{.....(76).}$$

Unlike integration, the factor 2r which appears in the equation, is now multiplicative and thus gives rise to a loss of accuracy which is invariably pr[illegible]tion.

3.5.4 Calculation of Chebyshev coefficients

3.5.4 Calculation of Chebyshev coefficients

This method is only suitable where, for prescribed equally spaced values of x, values of f(x) can be easily obtained, either by evaluating f(x) or from tables. The formula used to calculate the coefficients a_r for the equation (70) is

$$a_r = \frac{2}{n} \sum_{j=0}^{n}{}'' f(\cos \frac{\pi j}{n}) \cdot \cos \frac{\pi r j}{n} \qquad \text{.....(77).}$$

CHAPTER 4

THERMODYNAMIC THEORY

4.1 Introduction

The science of thermodynamics deals with relations between heat and work. It is based on two general laws of nature, the first and second laws of thermodynamics. By logical reasoning from these laws it is possible to correlate many of the observable properties of matter, such as coefficients of expansion, compressibilities, specific heat capacities and vapour pressures.

Thermodynamics makes no hypotheses about the structure of matter. It is an experimental or empirical science, and thermodynamic formulae necessarily have the same general validity as the two laws from which they are derived. The price of generality is a restriction in scope. Thus thermodynamics can predict many relationships between properties of matter but not the actual magnitude of these properties.

Hence, once an equation of state has been established for a substance it is then possible by using the thermodynamic relations to calculate the remaining properties. The accuracy with which they are calculated depends entirely on the accuracy of the original equation of state, which in turn depends on the accuracy of the experimental data on which it was based. From this argument it follows that an equation of state must not only provide close agreement with the measured values used in its correlation but also that its derived values must also agree with the experimental data.

There are however some properties which it is almost impossible to measure e.g. entropy, internal energy while there are others for which it is comparatively simple to provide accurate measurements e.g. pressure, temperature. The quantities which are measured in almost every experiment are p and T, while the following are the others which are most commonly measured; volume, enthalpy, specific heat at constant pressure, the Joule-Thomson coefficient $(\frac{\partial v}{\partial p})_T$, speed of sound.

However, before carrying out any work on equations of state for water substance

it is necessary to be familiar with the different phases as expressed on a p-v-T diagram, the thermodynamic relationships among the properties and the different temperature scales. These subjects will now be dealt with in turn.

4.2 p-v-T surface for water substance

Study of the p-v-T surface shows that there are certain regions in which the substance can exist in a single phase only. These are the solid, liquid and gas or vapour phases. The other regions are two-phase and are the solid-liquid, solid-vapour and liquid-vapour and they can be seen quite clearly on the projection of the surface onto a p-T plane (fig 2). The point where all three phases coincide is called the triple point. Where the liquid and vapour can exist in equilibrium, the vapour is called a saturated vapour and the liquid is a saturated liquid and together they compose the saturation line. The pressure applied by a saturated vapour or liquid is called the vapour pressure. The point on the saturation curve where the liquid and vapour values are equal and $(\frac{\partial p}{\partial v})_T = (\frac{\partial^2 p}{\partial v^2})_T = 0$ is called the critical point.

In the past the critical constants p_c, t_c, v_c have been calculated by the following two methods.

The first is by substitution into one of the ideal gas equations. If for example van der Waal's equation, (25), is chosen, then by application of the above condition the following critical values are obtained;

$$v_c = 3b; \quad T_c = \frac{8a}{27Rb}; \quad p_c = \frac{a}{27b^2}$$

This method is very simple but due to the lack of precision displayed by this type of equation it is also very inaccurate.

The second is the method of rectilinear diameters. Here the liquid and vapour volumes (or any other property) are plotted on a v-T graph (fig 3) and the mean of the volumes, $\frac{1}{2}(v_f + v_g)$, drawn in.

Then the point of intersection of the saturation curve and the mean diameter will give the critical point. This method allows for far greater precision and will also allow a reasonable estimate of the error involved.

Now the terms 'gas' and'vapour' have been used without distinguishing between them although the distinction is in fact quite arbitrary. A gas is a substance in its gaseous state at a temperature above its critical temperature while a vapour, implying the possibility of liquifaction, is a substance in its gaseous state at a temperature below its critical temperature. These two terms however are only rarely used in the strict sense of their definition.

Now that the existence of the solid phase has been described it will not be alluded to further since it is not of general interest. Similarly the sublimation curve (the solid-vapour boundary) and the melting curve (the solid-liquid boundary) are here of less importance although equations for them have been devised by Stein (59).

Hence the only regions of water substance which are of real interest are the saturation line, the liquid and vapour phases, all of which will be discussed in the course of this thesis.

4.3 Relationships

Before defining and calculating the thermodynamic relationships it is necessary to obtain the various mathematical relations which will be required.

4.3.1 Relations between partial derivatives

Suppose that there are three variables satisfying the equation

$$z = z(x, y)$$

then the following relations hold

$$\left(\frac{\partial x}{\partial y}\right)_z = 1/\left(\frac{\partial y}{\partial x}\right)_z \qquad \text{.....(78)}$$

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1 \qquad \text{.....(79)}$$

The order of successive differentiation of z(x, y) is immaterial. Hence

$$\frac{\partial}{\partial x}\frac{\partial z}{\partial y} = \frac{\partial}{\partial y}\frac{\partial z}{\partial x} \qquad \text{.....(80)}$$

Similarly for the equation w = w(x,y) where the variable x may be expressed

by $x = x(y, z)$ then

$$\left(\frac{\partial w}{\partial y}\right)_z = \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial w}{\partial x}\right)_y + \left(\frac{\partial w}{\partial y}\right)_x \qquad \text{.....(81)}$$

and

$$\left(\frac{\partial w}{\partial z}\right)_y = \left(\frac{\partial w}{\partial x}\right)_y \left(\frac{\partial x}{\partial z}\right)_y \qquad \text{.....(82)}$$

4.3.2 Thermodynamic relations

These are all based on the First and Second Laws of Thermodynamics which may be written as follows:

First Law: $dq = du + pdv$ .....(83)

Second Law: $dq = Tds$ .....(84)

By definition: $h = u + pv$ .....(85)

$f = u - Ts$ .....(86)

$g = u - Ts + pv = h - Ts$ .....(87)

Hence from equations (83) and (84)

$$du = Tds - pdv \qquad \text{.....(88)}$$

By differentiation of equations (85) to (87) and substitution for du from equation (88)

$$dh = Tds + vdp \qquad \text{.....(89)}$$

$$df = -sdT - pdv \qquad \text{.....(90)}$$

$$dg = -sdT + vdp \qquad \text{.....(91)}$$

By using the cross-differentiation identity given in equation (80), Maxwell's Relations may be calculated from equations (88) to (91). They are

$$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial p}{\partial s}\right)_v \qquad \text{.....(92)}$$

$$\left(\frac{\partial T}{\partial p}\right)_s = \left(\frac{\partial v}{\partial s}\right)_p \qquad \text{.....(93)}$$

$$\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p \qquad \text{.....(94)}$$

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v \qquad \text{.....(95)}$$

The following relations can be obtained simply from the above equations.

$$\left(\frac{\partial u}{\partial v}\right)_s = \left(\frac{\partial f}{\partial v}\right)_T = -p \qquad \text{.....(96)}$$

$$\left(\frac{\partial u}{\partial s}\right)_v = \left(\frac{\partial h}{\partial s}\right)_p = T \qquad \text{.....(97)}$$

$$\left(\frac{\partial f}{\partial T}\right)_v = \left(\frac{\partial g}{\partial T}\right)_p = -s \qquad \text{.....(98)}$$

$$\left(\frac{\partial h}{\partial p}\right)_s = \left(\frac{\partial g}{\partial p}\right)_T = v \qquad \text{.....(99)}$$

However, if any further relationships are required then they can be obtained from these equations.

4.3.3 Saturation relations

There are a few extra properties which are valid only for the saturation line which will now be described. The first of these relations is the Clausius-Clapeyron relationship:

$$\frac{dp}{dT} = \frac{s_g - s_f}{v_g - v_f} = \frac{h_g - h_f}{T(v_g - v_f)} \qquad \text{.....(100)}$$

The properties which are peculiar only to the saturation line are the calorimetric observations, based on principles laid down by Osborne (28). Only three of those experiments are of any concern.

The first is the quantity defined by Osborne as α, a symbol which it is convenient to retain along with the quantities β' and γ, defined below. The quantity, α, is a close approximation to the heat capacity of saturated liquid water, particularly at the lower temperatures. It may be shown that

$$\alpha = h_f - v_f T\frac{dp}{dT} \qquad \text{.....(101)}$$

$$\beta' = v_f T\frac{dp}{dT} \qquad \text{.....(102)}$$

$$\gamma = v_g T\frac{dp}{dT} \qquad \text{.....(103)}$$

These equations may be combined to give

$$h_f = \alpha + \beta' \qquad \text{.....(104)}$$

and $$h_g = \alpha + \gamma \qquad \text{.....(105)}$$

by using equation (100).

Now equation (89) may be rewritten

$$ds = \frac{dh}{T} - \frac{v}{T}.dp$$

and since

$$\frac{dh}{T} = d\left(\frac{h}{T}\right) + \frac{h}{T^2}\,dT$$

then

$$ds = d\left(\frac{h}{T}\right) + \frac{h}{T^2}\,dT - \frac{v}{T}\,dp$$

If this equation is applied to the saturated liquid then

$$ds_f = d\left(\frac{h_f}{T}\right) + \frac{h_f}{T^2}\,dT - \frac{v_f}{T}\,dp \qquad \text{.....(106)}$$

Equation (106) may be reduced using equation (101) to give

$$ds_f = d\left(\frac{h_f}{T}\right) + \frac{\alpha}{T^2}\,dT \qquad \text{.....(107)}$$

Integration of equation (107) gives the entropy of the saturated liquid as

$$\left[s_f\right]_{T_o}^{T} = \left[\frac{h_f}{T}\right]_{T_o}^{T} + \int_{T_o}^{T} \frac{\alpha}{T^2}\,dT + c \qquad \text{.....(108)}$$

where c is a constant of integration depending on the datum state, T_o, used. In chapter 5, the triple point, T_t, is always used as the datum state and since $s_f = 0$ there, by definition, c is always zero for this condition.

For the saturated vapour

$$s_g = s_f + \frac{h_{fg}}{T} \qquad \text{.....(109)}$$

4.3.4 Relations for less important properties

Some of the less used properties - coefficients of expansion, compressibilities etc., will now be described and defined.

The first of these is the coefficient of thermal expansion, α_p, defined by

$$\alpha_p = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p \qquad \text{.....(110)}$$

This property is also expressed in particular form for the saturation line by

$$\alpha_\sigma = \frac{1}{v}\left(\frac{dv}{dT}\right)_\sigma \qquad .....(111)$$

The isothermal coefficient of bulk compressibility is expressed by

$$\beta_T = \frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T \qquad .....(112)$$

but its saturation coefficient β_σ is of little importance.

The thermal pressure coefficient, γ_v, is the last of the p-v-T derivatives and is given by

$$\gamma_v = \left(\frac{\partial p}{\partial T}\right)_v \qquad .....(113)$$

and

$$\gamma_\sigma = \left(\frac{dp}{dT}\right)_\sigma \qquad .....(114).$$

These three coefficients are repeated as adiabatic coefficients i.e. derivatives for constant entropy.

$$\beta_s = \frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_s \qquad .....(115)$$

$$\gamma_s = \left(\frac{\partial p}{\partial T}\right)_s \qquad .....(116)$$

$$\alpha_s = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_s \qquad .....(117).$$

There are three heat capacities which will now be mentioned. The first c_σ, is more closely related to experiments than either c_p or c_v.

$$c_\sigma = T\left(\frac{ds}{dT}\right)_\sigma \qquad .....(118)$$

$$c_p = c_\sigma + T\left(\frac{\partial v}{\partial T}\right)_p \left(\frac{dp}{dT}\right) \qquad .....(119)$$

$$c_v = c_\sigma - T\left(\frac{dv}{dT}\right)_\sigma \left(\frac{\partial v}{\partial T}\right)_p \Big/ \left(\frac{\partial v}{\partial p}\right)_T \qquad .....(120).$$

The last property which is of any importance is the velocity of sound, W, which is obtained from

$$W^2 = v/\beta_s \qquad .....(121)$$

4.4 Temperature scales

The problem of temperature scales is complicated by the small changes in the definitions of the basic measures. However this difficulty would now appear to have been overcome in a scientific manner at the 13th Conférence Générale des Poids et Mesures (CGPM) in Paris in October 1967.

There are two basic measures of temperature. The first is the Thermodynamic Temperature, T, which arises, ~~as shown by Haywood (60)~~, as a corollary of the Second Law of Thermodynamics. In the Système International d'Unité (SI unit) the unit of thermodynamic temperature is the kelvin, and is obtained by assigning to the temperature level at the triple point of ordinary water substance, the exact number 273.16. Thus the definition for the unit of thermodynamic temperature, the kelvin, may be expressed using the terminology of Le Fevre (61) thus:

The kelvin unit of thermodynamic temperature, here named the kelvin and given the unit symbol K, is defined as $^1/273.16$ of the thermodynamic temperature in kelvins, at the triple point of ordinary water substance.

However since the measurement of thermodynamic temperature is extremely difficult it is used only in the thermodynamic relationships.

The second is an empirical scale temperature which is very suitable for making experimental measurements. This is called the International Practical (Celsius) Scale of Temperature, (IPTS), which assigns exact numbers to certain accurately reproducible temperature levels. It is not possible to quote the full statement of the IPTS but two important fixed points are the triple point of water, 0.01 ^{o}C exactly and the steam point, 100 ^{o}C exactly at a pressure of 1.01325 bar exactly. The unit on this scale is almost equal in size to a kelvin unit and for practical purposes 'thermodynamic temperatures' may be obtained by adding 273.15 to the IPTS value or in symbols

$$T\ ^{o}K = t\ ^{o}C + 273.15.$$

These two measures of temperature, because of their definitions, can neither be identical nor be related by some simple formula. The difference

between the two temperatures has been measured at a number of fixed points. These differences and the derivative $\frac{dt}{dT}$ were calculated by Bridgeman and Aldrich (62) using the equation

$$T - \tau = \frac{t}{t_{100}}\left[-0.006 + \left(\frac{t}{t_{100}} - 1\right)(0.04106 - 7.363\times10^{-5}\ t)\right] \qquad .....(122)$$

adopted by the 11th CGPM in 1960.

Two equations based on his own appraisal of the data have been calculated by Ferguson (63). They are

for the range $0\ ^{o}C \leq t < 630.5\ ^{o}C$

$$T - \tau = -4.1637501\times10^{-4}\ t + 3.3995852\times10^{-6}\ t^2 + 4.7805973_{10}{}^{-9}\ t^3 - 3.7865610\times10^{-11}\ t^4 + 3.8808209\times10^{-14}\ t^5 \qquad .....(123a)$$

and for the range $630.5\ ^{o}C \leq t \leq 1063\ ^{o}C$

$$T - \tau = -24.822595 + 8.5927954\times10^{-2}t - 9.6569016\times10^{-5}t^2 + 3.6583805\times10^{-8}t^3 \qquad ...(123b)$$

The differences and derivatives obtained from these equations are in fairly good agreement as can be seen from the entries in Table 1. In the past the difference between the two temperature scales has been neglected as it was considered to be negligible. However in the course of this work it was felt that the difference might be more significant than had been previously thought and so the following investigation was carried out.

4.4.1 Effects of the different temperature scales

It has been shown that there exists a difference between the two temperatures - thermodynamic and IPTS - and it is of considerable interest to discover what difference this makes in the calculation of the various properties. The saturation properties will be dealt with first.

The equations which are correlated in Chapter 5 are assumed to be functions of the IPTS since they are based mainly on experimental results. However, whether this is actually the case or not, it is necessary to make that assumption as a basis for further calculations. The temperatures will be represented by the following symbols:

IPTS: $\tau\ ^{o}K = t\ ^{o}C + 273.15$

Thermodynamic (THERM): T K

and the properties will use IPTS as a subscript to denote that they are based only on that scale whereas lack of a subscript is taken to mean the true value, e.g. β'_{IPTS} and β'.

4.4.2 Saturation properties

Now the properties p, v_f, α, h_g are defined to be on the IPTS since they are all obtained from the equations in Chapter 5 i.e. they are all functions of τ. The first property to be calculated is β' using equation (102) which may be modified to

$$\beta' = v_f T \frac{dp}{dT}$$

$$= v_f \tau \frac{dp}{d\tau}\left(\frac{T}{\tau} \cdot \frac{d\tau}{dT}\right)$$

$$= v_f \tau \frac{dp}{d\tau} \cdot \omega$$

$$\text{where } \omega = \frac{T}{\tau}\frac{d\tau}{dT}$$

But if the relation was used, substituting τ for T then

$$\beta'_{IPTS} = v_f \tau \frac{dp}{d\tau}$$

Hence the difference $\Delta\beta'$ caused by the difference in temperature scale may be written

$$\Delta\beta' = \beta' - \beta'_{IPTS} = (\omega-1)\ \beta'_{IPTS} \qquad .....(124)$$

Similarly from equation (104)

$$h_f = \alpha + \beta'$$

$$h_{f_{IPTS}} = \alpha + \beta'_{IPTS}$$

$$\text{Hence } \Delta h_f = h_f - h_{f_{IPTS}} = \beta' - \beta'_{IPTS} = \Delta\beta' \qquad .....(125)$$

From equation (108), $s_f = \frac{h_f}{T} + \int \frac{\alpha}{T^2}\, dT$

Now from equation (123), $\frac{dT}{d\tau} = F(\tau)$

and hence $dT = F(\tau)d\tau$

however $F(\tau)$ is very nearly constant and equal to unity and so it may be neglected. Thus it is possible to write, where $\kappa = \frac{\tau}{T}$

$$s_f = \frac{h_f}{\tau} \kappa + \int \frac{\alpha}{\tau^2} \kappa^2 \, d\tau$$

$$= \frac{h_f}{\tau} \kappa + \kappa^2 \int \frac{\alpha}{\tau^2} d\tau$$

since κ^2 may be considered to be constant without any great loss of accuracy.

$$s_{f_{IPTS}} = \frac{h_{f_{IPTS}}}{\tau} + \int \frac{\alpha}{\tau^2} \kappa^2 d\tau$$

Thus $\Delta s_f = s_f - s_{f_{IPTS}} = \frac{h_f}{\tau} \kappa - \frac{h_{f_{IPTS}}}{\tau} + (\kappa^2 - 1) \int \frac{\alpha}{\tau^2} d\tau$

$$= \frac{\kappa(1-\kappa)}{\tau} h_{f_{IPTS}} + \frac{\kappa}{\tau} \Delta h_f + (\kappa^2 - 1) s_{f_{IPTS}} \qquad .....(126)$$

Now $\gamma = h_g - \alpha$

and so since h_g and α are corrected values γ will be also.

From equation (103), $v_g = \gamma/T \frac{dp}{dT}$

$$= \gamma/\tau \frac{dp}{d\tau} \omega$$

and $v_{g_{IPTS}} = \gamma/\tau \frac{dp}{d\tau}$

Hence $\Delta v_g = (\frac{1}{\omega} - 1) v_{g_{IPTS}}$ .....(127)

Finally from equation (109), $s_g = s_f + \frac{h_{fg}}{T} = s_f + \frac{h_{fg}}{\tau} \cdot \kappa$

$$s_{g_{IPTS}} = s_{f_{IPTS}} + \frac{h_{fg_{IPTS}}}{\tau}$$

Hence $\Delta s_g = s_{f_{IPTS}} + \left[(h_g - h_{f_{IPTS}} - \Delta h_f)\kappa - (h_g - h_{f_{IPTS}})\right]/\tau$

$$= \Delta s_f + \left[(h_g - h_{f_{IPTS}})(\kappa - 1) - \kappa \Delta h_f\right]/\tau \qquad .....(128)$$

The quantities, expressed by equations (124) to (128), have been calculated for various temperatures and are compared in Table 2 with the IST values and the tolerances for h_f and v_g and in the other cases with the table entries from

Appendix IV for β', s_f and s_g. It is evident, in particular for v_g, that if the tolerance has any significance then the difference in the temperature scales must be taken into account. This is true for the saturation line and it only remains to show that this also holds for the general case.

One further argument is supplied by a comparison of the difference $(T - \tau)$ with the tolerance on temperature at the critical point. The values are given in Table 1 and it is at once obvious that the difference $(T - \tau)$ is slightly larger than the tolerance of $\pm$ 0.10 C^o. It is thus seen that the uncertainty in the critical temperature, and the other critical values, cannot be reduced unless the difference in the temperature measures is acknowledged.

4.4.3 Water and Steam

If it is assumed that an equation of state for water substance of the form $p = p(v, \tau)$ exists then it is possible to calculate the difference in entropy and enthalpy caused by the different scales. Now using the symbols of the previous section and the relationships derived in section 4.3.2 it is possible to calculate Δs and Δh.

$$s = -\int \frac{\partial p}{\partial T}\, dv$$

$$= -\frac{d\tau}{dT} \int \frac{\partial p}{\partial \tau}\, dv$$

$$\text{and } s_{IPTS} = -\int \frac{\partial p}{\partial \tau}\, dv$$

$$\text{Hence } \Delta s = s - s_{IPTS} = \left(\frac{d\tau}{dT} - 1\right) s_{IPTS} \qquad \ldots\ldots(129)$$

It is simpler to rewrite this equation, since it is only temperature-dependent, as

$$\%\Delta s = \frac{\Delta s}{s_{IPTS}} \times 100\% = \left(\frac{d\tau}{dT} - 1\right) \times 100\%$$

and to give the values of $\%\Delta s$ for different values of t. This is done in Table 3. Similarly, enthalpy is calculated from

$$h = -\int p\,dv + pv - T \int \frac{\partial p}{\partial T}\, dv.$$

Since the only part of this equation which is dependent on temperature is the last term, then if it is replaced by Y the following is obtained.

$$Y = -T \int \frac{\partial p}{\partial T} dv = -\frac{T}{\tau}\frac{d\tau}{dT} \cdot \tau \int \frac{\partial p}{\partial \tau} dv$$

$$\text{and } Y_{IPTS} = -\tau \int \frac{\partial p}{\partial \tau} dv$$

$$\text{Hence } \Delta h = h - h_{IPTS} = Y - Y_{IPTS}$$

$$= \left(\frac{T}{\tau}\frac{d\tau}{dT} - 1\right)\tau \int \frac{\partial p}{\partial \tau} dv$$

$$= (\omega - 1)\, \tau\, s_{IPTS} \qquad .....(130)$$

In order to compare the values of Δh with the IST tolerance, Table 3 has been drawn up. It can be seen from the points chosen for this table that in some regions - in particular low pressure, high temperature - almost half the tolerance will be taken up.

This point is of particular importance since in some cases the real uncertainty on the given property may be about one-third of the tolerance as stated in the 1963 IST. This is caused by two factors. The first is that when the 1963 IST were formed a very generous allowance was made in estimating the tolerance to allow for any systematic errors in the experimental data and the second is that new and more accurate measurements made since then confirm that in certain regions, the tolerances are too large by a factor of two or three. This emphasises yet again that the difference in temperature scales must be allowed for.

However although the difference between the thermodynamic and Practical temperatures has been shown to be significant no account will be taken of it in the preparation of tables or equations in this work since all the data upon which this thesis is based must already have this error inherent in it. Thus the obvious solution is that in any future work the difference in the temperature scales must be allowed for, especially if greater accuracy is required.

CHAPTER 5

THE SATURATION LINE

5.1 Introduction

The saturation line is very important as it provides the boundary between the liquid and vapour regions. Due to this importance it was felt necessary to unify the final results of Osborne, Stimson and Ginnings (22) by providing equations to replace the untidy mixture of tables and correlations upon which their final and definitive paper was based. The provision of these equations permits evaluation of all the state properties along the saturation line from the triple point to the critical point, thus providing the most important boundary, with the exception of the hypothetical gas curve, for any surface which purports to represent the thermodynamic properties of water in its liquid and vapour phases. In view of the rigour with which earlier work was reviewed by Osborne and his colleagues, only work relating to the saturation line published since 1939 is considered. The work on the saturation properties at the NBS was carried out over the period 1930 to 1939 and their results and critical reviews of earlier work was published in a number of papers, which due to their importance, are listed in reference (64). The final paper by Osborne, Stimson and Ginnings summarises in tabular form the results of all the investigations and this paper must be considered as definitive. These results were taken directly by Bain in 1964 and used to compile the tables of saturation properties in the NEL Tables (65). All the equations formulated in this chapter have been calculated using data from the latter source.

However, none of the correlations provided at the NBS are suitable for use with an h - s - p formulation. The only reasonable form of saturation equation for this surface would have to be expressed using any two of the variables enthalpy, entropy or pressure and this problem will be dealt with first before tackling the more general one of finding equations which will

specify all the saturation properties with thermodynamic consistency.

5.2 Saturation equation for use with an h - s - p formulation

This part of the work was undertaken in collaboration with R.I. McLeod at the National Engineering Laboratory, East Kilbride, who was attempting to produce a single equation of the form s = s(h, p) to cover both liquid and vapour regions. An exploratory study of the problems which would arise in the pursuit of the task was undertaken by Haywood and Bott (42) at Cambridge University in 1964. They concluded that for the purpose of providing a boundary between the liquid and vapour phases in a s - h - p formulation, the saturation equation could not be represented by a p - t equation but it must be in any two of the variables s, h or p. From graphs that they drew, and replotted in figs. 4, 5 and 6 they concluded that an equation of the form s = s(ln p) would have the best chance of providing an adequate fit, although there appeared to be an inflexion in the steam curve between p = 1 and p = 10 bar. They carried out one fit of the saturated steam curve which, with the exception of the vicinity of the critical point, produced an adequate fit.

One difficulty in providing the saturation boundary was whether one equation would suffice or whether two would be necessary. On looking at the graphs it appeared much simpler and easier to use two equations: one for the water and one for the steam.

5.2.1 Vapour entropy equation

This equation was dealt with first as Haywood and Bott had provided a fit to it. However this equation was not adequate in the region of the critical point. The general form of the equation is

$$s_g = \sum_{r=0}^{n}{}' A_r T_r(m) \qquad \text{.....(131)}$$

where $m = (2x - A - B)/(B - A)$

and x is the particular form of the dependent variable p.

The data used in the curve fitting was taken from Table 1 of the NEL Tables for temperatures from 0 °C by 1 deg to the critical point (i.e.377 entries).

In order to demonstrate the usefulness of graphs in curve fitting problems, the vapour entropy was fitted as a function of pressure i.e.

$$x = p \text{ ——— (i)}$$

The results of this fit can be seen in the first line of Table 4. The data was fitted up to a power of n = 15 using form (i) and it was found that the fit with 12 coefficients provided the best approximation to the data. In other words even if more than 12 coefficients were used there was no significant decrease in the standard deviation. For all the correlations in the table the maximum deviations along with the values of pressure at which they occurred are tabulated so that the different equations may be easily compared.

The next form of the dependent variable used

$$x = \ln \beta \text{ ——— (ii)}$$

was, from graphical considerations, expected to provide an improved fit. This, as can be seen, was the case and an interesting point worth noting is that with the first fit, the largest deviations occurred at the low pressures where the accuracy of the data should be best while with the second form the largest deviations occurred in the region of the critical point. In fact, on looking at the maximum percentage deviations it is much more reasonable to find an error in the critical value of 4% than one of 10% at the triple point.

Since the entropy values were obtained by calculation and not by experiment the accuracy with which they should be fitted can only be estimated. Hence, all that can be said in advance about the accuracy of the fit is that it cannot be any better than one figure in the last decimal place due to rounding error, i.e. for values of entropy expressed in J/g K the maximum error cannot be less than 0.001 J/g K and any fit obtained within 0.002 J/g K at all points will be more than adequate, while more precise values are lacking.

It was at this stage in the work that McLeod suggested that if the form $x = (\ln p)^k$ was used where k was about 0.4 a much improved fit would be obtained.

He had reached this conclusion by plotting ln s_{fg} against ln ln p and finding that it turned out to be very near a straight line with a gradient very close to 0.4. Thus it is possible to write, where k is the gradient,

$$\ln s_{fg} = k \ln \ln p + C$$

$$= \ln (\ln p)^k + \ln c$$

$$= \ln c(\ln p)^k$$

$$\therefore s_{fg} = c(\ln p)^k$$

However, instead of plotting p it was decided to use the dimensionless form β but this meant that $(\ln \beta)^k$ would be negative and so $\ln(1/\beta)$ was used instead and a plot of ln s_{fg} against ln $\ln(1/\beta)$ is given in fig. 7. In other words the form $x = \{\ln(1/\beta)\}^k$ ——— (iii) was used since the powers of the constant c can be included in the coefficients.

This relation applies to s_{fg} but it might also be applicable to s_g and s_f. However it is necessary to have one of these latter relations, since an equation for s_{fg} will not enable either s_f or s_g to be calculated without more information. But if for example, equations for s_f and s_{fg} are given then in order to obtain s_g both equations must be evaluated. For this reason it was decided to fit both s_g and s_f.

Using form (iii) further correlations were carried out using different values of k and on examining the results as expressed in Table 4 it was immediately obvious that the equation with k = 0.3 satisfied all the necessary criteria about accuracy as well as using the smallest number of coefficients.

Hence the vapour entropy equation is written

$$s_g = \sum_{r=0}^{9}{}' A_r T_r(m) \qquad \text{.....(132)}$$

where $m = 1 - A_{10} \left[\ln (1/\beta)\right]^{0.3}$

A comparison of the values obtained from equation (132) with those from the NEL tables is made in Table 5 and the coefficients are given in Appendix II.

5.2.2 Liquid entropy equation

This equation was calculated in an identical fashion to the vapour entropy equation only in this case the best value of k was 0.2 as can be seen from the results in Table 6. However on looking at these results more closely it is immediately obvious that there is a further problem. This is due to the definition of $s_f = 0$ at the triple point i.e. where $p = 0.006112$. Naturally it is not possible to obtain the percentage deviation at this point and so it is not given. But in each case the percentage deviation is largest at zero temperature where $s_f = -0.0002$ i.e. at $p = 0.006107$ and hence since these points are so close together they will have almost identical deviations. On evaluating the equation (133) for these values, it could be seen that $s_f = -2.78_{10}{}^{-5}$ at the triple point. This would be permissible.

However there is one method, which is much simpler and easier than either weighting or constraints for modifying the equation such that the liquid entropy will be zero exactly at the triple point.

The equation with which this fit was obtained is

$$s_f = \sum_{r=0}^{7}{}' B_r T_r(m) \qquad \text{.....(133)}$$

where $M = 1 - B_0\left[\ln\left(1/\beta\right)\right]^{0.2}$.

It may ofcourse be expanded to give a constant term of $B_o/2$ and if we assume $s_f = \Delta$ at $t = 0.01\ ^oC$ then by adding $-\Delta$ onto the constant term s_f would be zero exactly at the triple point. The advantage of this method is that it only requires a very minor alteration to B_o which does not significantly affect the other values of s_f. Hence the new value of the constant would be $B_o - 2\Delta$ i.e. $\Delta B_o = -2\Delta$.

Therefore since $\Delta = -2.781548_{10}{}^{-5}$ then $\Delta B_o = 5.563096_{10}{}^{-5}$. The values of the coefficients are given in Appendix II with the new value of B_o inserted such that the triple point value of s_f is zero exactly.

5.3 Vapour pressure of saturated water

The saturation line is defined by the pressure-temperature measurements made at the National Bureau of Standards (NBS) and at the Physikalisch-Technischen Reichsanstalt (PTR) and which have been closely approximated by two equations. The first was devised by Dr. H.T. Gerry of the NBS to cover the temperature range 0 °C to 100 °C and is based on the revised measurements of Holborn and Henning (14) at the PTR. The second equation, which is valid from 100 °C up to the critical temperature, was correlated by Osborne and Meyers (21) from the NBS measurements. These two equations were used to provide the input data for the vapour pressure correlation.

The vapour pressure equation is the one where pressure is the independent variable i.e. $p = f(t)$ and will also be referred to as the primary equation as opposed to the reverse form $t = f(p)$ which will be termed the supplementary equation.

5.3.1 Vapour pressure equation

From the many equations examined in Chapter 1 it appeared that if the variables were expressed in the form ln p as a function of $^1/T$ then a reasonable fit might be obtained. Some preliminary investigation of possible forms of the variables was then conducted graphically and the relevant ones are reproduced in figs. 8, 9 and 10. The first forms examined were $p - t$ and $\ln p - t$ (fig 8) but neither of these gave straight line curves. The other graphs were all plotted using the inverse of β, the dimensionless form of pressure to enable the graphs to be plotted down to zero temperature. When $\ln {}^1/\beta$ against $^1/T$ was plotted (fig 9a) the result was very close to a straight line. On taking logarithms of both sides and replotting the results were not nearly so encouraging. However, a form of variable which had been used by Smith and Keyes (27) amongst others was $(t_c - t)$ and this suggested the form $^1/\beta$ against $(\frac{1}{T} - \frac{1}{T_c})$. On this form being expressed graphically it was immediately obvious

(fig 10) that this was the best form of the equation.

Basing the correlating equations on these graphs the following forms of the variables were fitted in turn:

$$p = f\{t\} \qquad \text{——— (iv)}$$

$$\ln p = f\{t\} \qquad \text{——— (v)}$$

$$\ln p = f\{(1/T)^k\} \qquad \text{——— (vi)}$$

$$\ln p = f\{(\frac{1}{T} - \frac{1}{T_c})^k\} \qquad \text{——— (vii).}$$

The results obtained by fitting these equations are tabulated in Table 7. As expected forms (iv) and (v) are not very successful and form (vi) with $k = 1$ is very poor indeed, but with $k \leq 0.5$ it proves much more effective. When form (vii) is examined it is seen that it is even better and that the best fit so far is (vii) with $k = 0.4$. In all the fits attempted, the optimum number of coefficients appeared to be about 12 and so, in order to simplify comparison and calculation, this number of coefficients is used unless otherwise stated.

When this equation was evaluated for all the skeleton table points it was seen that it provided an excellent fit well within the tolerances with the exception of $t = 100\ ^{o}C$ where due to the very small tolerance the equation would need to be weighted or constrained. The derivative $T\frac{dp}{dT}$ was next evaluated in order to confirm that the values obtained were smooth and in reasonable agreement with those of other workers. It was found that for $T = T_c$, $(T\frac{dp}{dT})_c = 0$ which was not in agreement with the results of Osborne, Stimson and Ginnings who obtained $(T\frac{dp}{dT})_c = 173.13\ cm^3/J$. In order to understand why this came about it is necessary to show how the derivative is obtained. The form (vii) of the equation is written:

$$Y = \ln p = \sum_{r=0}^{n}{}' a_r T_r(x) \qquad \text{.....(134)}$$

where $x = (2y - A - B)/(B - A)$

and $y = (\frac{1}{T} - \frac{1}{T_c})^k$

$$\therefore T\frac{dp}{dT} = T \cdot \frac{dp}{dY} \cdot \frac{dY}{dx} \cdot \frac{dx}{dy} \cdot \frac{dy}{dT}$$

$$= T \cdot p \cdot \frac{dY}{dx} \cdot \frac{2}{B-A} \cdot k \cdot \left(\frac{1}{T} - \frac{1}{T_c}\right)^{k-1} \cdot \left(\frac{1}{T^2}\right)$$

$$= -\frac{p}{T} \cdot \frac{2k}{B-A} \cdot \frac{dY}{dx} \cdot \left(\frac{1}{T} - \frac{1}{T_c}\right)^{k-1}$$

Now $\frac{dY}{dx} = \sum_{r=0}^{n-1}{}' b_r T_r(x)$ and can be simply evaluated. Such that if we now evaluate the derivative for $T = T_c$ the factor $\left(\frac{1}{T} - \frac{1}{T_c}\right)^{k-1}$ immediately springs into prominence as it is equivalent to zero and thus forces the derivative to zero also.

There appeared to be two possible ways of tackling this problem. The first method tried was to extrapolate the curve to 380 ^{o}C and to take some extra points off the curve to be used in the curve fitting process. It was hoped that this might improve the derivatives near the critical point but only one or two fits were necessary to show that this method was completely useless as the derivative was not improved and the pressure values in fact deteriorated. The other method of surmounting this difficulty was to alter the form of the independent variable from $\left(\frac{1}{T} - \frac{1}{T_c}\right)$ to $\left(\frac{1}{T} - \frac{1}{T_c+K_1}\right)$ where K_1 is an arbitrary constant. A few fits were then undertaken using different values of K_1 and it was found that a positive value of the order of 25 should prove successful. Before continuing further it was thought advisable to make the equation dimensionless. To do this ln p was replaced by ln β, T by θ and the independent variable was altered as follows:

$$\left(\frac{1}{T} - \frac{1}{T_c+K_1}\right)^k = \left(\frac{1}{T_c}\right)^k \left(\frac{T_c}{T} - \frac{T_c}{T_c+K_1}\right)^k = K_2\left(\frac{1}{\theta} - C\right)^k .$$

The constant K_2 may be neglected as it will appear in the coefficients.
The approximate value of the constant C obtained is thus:

$$C = \frac{T_c}{T_c+K_1} = \frac{647.3}{647.3+25} = 0.96 .$$

The curve fitting process was now repeated using the form:

$$\ln \beta = f\left\{\left(\frac{1}{\theta} - C\right)^k\right\} \quad \text{(viii)} .$$

First of all, setting C = 1, the optimum value of k was confirmed to be 0.4, then with k = 0.4 the value of C was varied. There was very little difference

in the standard deviation or the deviations in pressure for the different values of C. However it was necessary to examine the value of the derivative at the critical point for the different values of C and the results are shown in Table 8. It is interesting to note that as C increases, $(T\frac{dp}{dT})_c$ increases to a maximum at C = 0.95, and then decreases to zero at C = 1. The likely explanation of this is as follows: The derivative $T\frac{dp}{dT}$ is written

$$T\frac{dp}{dT} = -\frac{2kT}{B-A}\cdot\frac{p}{T}\frac{dY}{dx}\cdot\left(\frac{1}{\beta}-C\right)^{k-1}$$

$$= X.Z$$

where $X = \frac{2kT_c}{(B-A)}\frac{p}{T}\frac{dY}{dx}$

and $Z = \left(\frac{1}{\beta}-C\right)^{k-1}$.

For C >0.95, Z is more significant than X, for C < 0.95 it is less significant than X and at C = 0.95 they are of roughly equal significance. Hence the best value of C must be 0.95.

Now using this equation there was a slight loss of accuracy compared with the best equation from form (vii) but the only value outside the IST tolerance was still only 100 °C. There are two possible ways of overcoming this problem. The first, which is exact, is by using constraints and would provide an equation of the form:

$$\ln\beta = \ln(P_{100}/P_c) + (t - t_{100})\sum_{r=0}^{n}{}' a_r T_r(x) \qquad \ldots\ldots(135).$$

However as Chebyshev polynomials are being used it is possible to include the factor $(t-t_{100})$ in the polynomial series which would enable the equation to be written thus:

$$\ln\beta = \ln(P_{100}/P_c) + \sum_{r=0}^{n+1}{}' b_r T_r(x)$$

and this could be simplified to

$$\ln P/P_{100} = \sum_{r=0}^{n+1}{}' b_r T_r(x) \qquad \ldots\ldots(136).$$

This last equation, though, does not have the dimensionless form of pressure (β) and if it was introduced it would only complicate the equation. This form also requires an extra coefficient and if possible it is preferable to keep the number of coefficients to an absolute minimum.

For these reasons it was decided to try to avoid the difficulty by using weights and only if this procedure proved ineffective would constraints be used. The use of weights does not require any alteration either to the

variables or to the number of coefficients. Various combinations of weights were tried and it was found that a weight of 15 applied to the temperatures from 96 °C to 105 °C was required to obtain $p_{100} = 1.01325$.

The final form of the equation thus obtained is

$$\ln \beta = \sum_{r=0}^{11}{}' a_r T_r(x) \qquad \text{.....(137)}$$

$$\text{where } x = (2(\frac{1}{\theta} - 0.95)^{0.4} - a_{12})/a_{13} \quad .$$

The coefficients for this equation are tabulated together with the coefficients for all the other saturation equations in Appendix II. In order to demonstrate the accuracy of this equation a % deviation plot is shown in fig 11. In it $(p_{OSG} - p_{EQN}) \times 100/p_{OSG}$ is plotted against temperature and it can immediately be seen that the maximum deviation below 350 °C is 0.0015 % and above 350 °C it is slightly higher at 0.014 %. This proves that the data is fitted well within the bounds of any experimental errors in the original data.

The equation values are compared with the IST values and tolerances in Table 9 and the only temperatures where the difference $p_{IST} - p_{EQN}$ approaches the IST tolerance is at 374 °C and 374.15 °C. This is hardly surprising since there is considerable doubt as to the property values at the critical point. This matter will be discussed in detail in section 5.8 and will not be further alluded to here.

5.3.2 Supplementary equation

A supplementary equation was provided because it was felt much simpler to provide this equation than to carry out inverse interpolation on the vapour pressure equation. As this equatiion is just the reverse of equation (137) it appeared logical to use a similar form of variable i.e.

$$\frac{1}{\theta} = f\{(\ln {}^{1}/\beta)^{k}\} \qquad \text{———(ix).}$$

However the derivative of this equation is zero at the critical point and a slightly modified form of the independent variable is necessary. From the results of fitting

the primary equation a suitable form of the independent variable might be:

$$(\ln {}^{1}/\beta + c)^{k} = (\ln {}^{K}/\beta)^{k} \quad \text{where } c = \ln K.$$

However $\ln {}^{K}/\beta \geq 0$

$\therefore K \geq 1.$

This would therefore give an equation of the form

$$\frac{1}{\theta} = f\{(\ln {}^{K}/\beta)^{k}\} .$$

Fitting was carried out using different values of k and K and the results are shown in Table 10. With K = 1, the best value of k is either 0.5 or 0.4 according to the standard deviation but the latter gives smaller maximum deviations and should provide the better fit.

A value for K of 1.1 provides an adequate result even although in Table 8 the value of the derivative at the critical point for K = 1.1 is not quite the maximum it is very close to it. Thus the final form of the equation is

$$\frac{1}{\theta} = \sum_{r=0}^{11}{}' b_r T_r(y) \qquad \text{.....(136)}$$

$$\text{where } y = (2(\ln {}^{1.1}/\beta)^{0.4} - b_{12})/b_{13} .$$

This equation provides a close fit to the data (fig 12) as below 360 ^{o}C the largest deviation is 0.0012 C^{o}, while above 360 ^{o}C the largest deviation is greater by a factor of 10.

It has now been shown that both these equations represent the data very accurately but it is necessary to show how accurate these two equations are when used in conjunction. First of all the primary equation is used to calculate p_1 from T_1 and then using the secondary equation, T_2 is calculated and the difference between T_1 and T_2 can be seen. These values are given in Table 11 and the maximum value of $(T_1 - T_2)$ is 0.003 C^{o} and the maximum % deviation $\frac{(T_1 - T_2)}{T_1} \times 100$ is 0.003 %. Table 12 expresses the results when the equations are used in reverse and shows that the maximum deviation is 0.005 bar or 0.002 %.

These results only serve to emphasise the accuracy of these two vapour pressure equations when used either separately or together.

5.3.3 Vapour pressure equations based on 'Craigoe-Stimson' corrections

After the vapour pressure equations already described had been completed, it was discovered by Dr. Angus* that there existed more recent measurements, in the temperature range 0 °C to 100 °C, which were being widely used by chemists investigating the vapour pressure of organic substances. These values differ slightly from those given in the 1963 IST and are to be found correlated in Table 2-1-(1.01)-K of the American Petroleum Institute Research Project 44 (25). It was also discovered that some recent measurements were in conflict with both these sources. Dr. Angus and Dr. Bruges corresponded with the various interested parties and then completed a short note on the subject which they submitted to the 2nd IFC Meeting in Glasgow and resulted in the following clarification of the problem.

The API 44 table uses as a basis the saturation table values of the 1963 IST, generated from the 1934 correlation of Osborne and Meyers which was at that time considered valid from 0 °C to 374.15 °C, and added corrections derived from measurements made at the National Bureau of Standards in connection with a gas thermometry programme, by Stimson and Craigoe in 1942 and by Stimson and Wilson in 1948. These 'Craigoe-Stimson' corrections as they are known, have never been published nor has the work on which they are based, but they have received limited private circulation (66).

Table of 'Craigoe-Stimson' corrections

Temperature °C	Δp to be added atm. x 10^{-6}
0	0
25	39
50	74
60	75
80	47
100	0

More recently Douslin (67), using an inclined piston gauge, has made observations on the vapour pressure of water in the range 0 °C to 20 °C.

*Scientific Director, IUPAC, Thermodynamic Tables Project Centre, Imperial College, London.

His measurements differ from both the IST and the API 44 tables, the difference increasing with increasing temperatures, and being outside the IST tolerances at the higher temperatures of this range.

It was decided that there were reasonable grounds for preferring the API 44 since the equations do not merge well at temperatures just below 100 °C. Further, the measurements of Moser and Zmaczynski (68) between 73 °C and 130 °C are almost identical with the original PTR (14) (69) (70) observations and the correlation of Osborne and Meyers. Accordingly it was decided to use the API 44 values as 'input data' between 0 °C and 100 °C and the Osborne and Meyers correlation as input data from 100 °C to 374.15 °C and to fit a single equation to the two sets of data. The basic equation has the same form as equation (137) and a complementary equation similar to (138) was also correlated. The two sets of equations give virtually the same results except in the range 0 °C to 100 °C where the second set, which will be denoted by (137b) and (138b), give slightly higher pressures than the first set. A comparison of equations (137) and (137b) in Tables 13 and 14 shows this agreement very well for both pressure and the derivative $T\frac{dp}{dT}$. Fig 13 gives deviations of equation (137b) from the 1934 correlation of Osborne and Meyers as well as other pertinent differences. There is good agreement between API 44 and the Craigoe-Stimson values except at 25 °C where there is an unexplained difference of 4_{10}-6 bar, which may be due to 'smoothing' done originally by Meyers. Equation (137b) agrees with API 44 to within 0.3 N/m^2 except at 90 °C where the discrepancy is 0.8 N/m^2. As can be seen both the API 44 correlation and equation (137b) give smooth curves whereas the 1939 NBS equation of Gerry appears to be imperfect between 70 °C and 100 °C thus demonstrating yet again the poor merging of the two NBS (1939) equations, referred to above and also shown in figs 11 and 12.

It was decided not to attempt to improve the equation further since the values obtained were accurate enough for practical purposes and well within the limits of all except the most precise pressure measurements. It was also decided to recommend the use of equations (137b) and (138b) in preference to equations

(137) and (138), although the latter reproduce the 1963 IST almost exactly, while at the same time equations (137b) and (138b) give values within the bounds imposed by the tolerances and are equally valid. At temperatures above 100 °C both sets of equations give values which are indistinguishable.

5.3.4 Comparison of vapour pressure equations

Mention has already been made of the two vapour pressure equations devised at the NBS. Since then various other equations, which all have rather different advantages and disadvantages, have been suggested and used. It is interesting and instructive to make a comparison of the best of these equations with respect to the important criteria used in computer programming i.e. economy of storage, speed and ease of use. There are six equations which will be discussed: (1) Osborne, Stimson and Ginnings (OSG); (2) Steltz and Silvestri (39) (SS); (3) Bridgeman and Aldrich (62) (BA); (4) 1966 K function (47); (5) 1967 K function (48); (6) equation (137). The form of these equations, their derivatives and coefficients are all described in Appendix I.

In order to be able to draw comparisons between different equations it is necessary to apply the criteria mentioned above. They may also be expressed by the following more positive questions.

(a) How many equations and what range do they cover?

(b) Number of coefficients?

(c) Number of operations e.g. addition etc. to be performed in calculating one value?

It is very simple to evaluate the first two points but the third is slightly more complicated. Now the ideal correlation would be the one which required only one equation to cover the entire range, used a minimum number of coefficients, say approximately 6, had a minimum number of arithmetic operations with no procedures or complicated functions e.g. cosh, ln, exp, and provided exact agreement with the original data. Table 15 has been drawn up to try and show how well the equations correspond to these criteria and an examination

of the table provides a very good guide as to how well they are satisfied.

The number of arithmetic operations are tabulated and the total time taken for the calculation of one value is given as a multiple of the time taken for an addition. This is based on the time factors calculated using the Whetstone Algol compiler on the English Electric KDF 9 and given in Table 16. These times are only approximate as the times for any particular operation vary according to the size and number of digits of the numbers being operated on. This is true in particular when using the procedures for ln, exp and ↑ (this is the Algol symbol for a^b which is represented by a ↑ b) which use an iterative process.

Hence it is now possible to make an evaluation of the usefulness of the various equations based on the above criteria. The two equations of the NBS are not very suitable for use due to their form and the fact that together they require at least as much storage as any of the others without providing any benefit in speed. The equations of Steltz and Silvestri which are based on the results of Keenan and Keyes do not cover the full range although they are the fastest, with the exception of the 1967 K function. The equation of Bridgeman and Aldrich does not have any advantages. It takes a long time to calculate as it contains the function $\cosh^{-1}$ and moreover its values in the region 20 °C - 100 °C are slightly high (see Table 18) although still well within the IST tolerances.

From these comments it is obvious that none of these equations are particularly suitable for general use. Thus only the last three equations are left. They were all programmed for the computer in both the KDF 9 Assembly Language-User Code, and Algol and their calculation times are given in Table 17.

The programmes in User Code were written by Bradly of English Electric for a paper (71) which he has submitted to the 7th ICPS and the average times he obtained and given in Table 17, are reproduced from his paper.

From a comparison of the relative times, it can be seen that those

from Table 15 provide fairly good agreement with those obtained from the User Code programmes. However on comparing the times of the Algol programmes it is immediately obvious that the time taken for equation (137) is very much longer than for either of the other two, which is in direct conflict with the previous times. This anomaly can be explained by the difficulty of programming the summation of Chebyshev polynomials in Algol. Either arrays are used, which is very wasteful of time or else a large number of assignment statements would be required which is almost as wasteful. In order to elucidate the problem it is now written in full.

The summation of $y = \sum_{r=0}^{n}{}' a_r T_r(x)$ is expressed mathematically by

$$b_{n+2} = b_{n+1} = 0$$

$$b_r = 2x\, b_{r+1} - b_{r+2} + a_r \quad (r = n, n-1, \ldots, 1, 0)$$

$$y = (b_0 - b_2)/2$$

Programmed in Algol using arrays it would appear

```
b[n+2]:=b[n+1]:=0.0; x:=2.0×x;
for r:=n step -1 until 0 do
b[r]:=x×b[r+1]-b[r+2]+a[r];
y=0.5×(b[0]-b[2]);
```

Now if this was re-programmed to eliminate the arrays it would appear

```
Y:=Z:=0.0;  x:=2.0×x;
for r:=n step -1 until 0 do
begin X:=Y;  Y:=Z;
      Z:=x×Y-X+a[r];
end;
y:=0.5×(Z-X);
```

However when this problem is tackled in User Code, the second method suitably modified would provide the basis of the programme. None of the assignment statements would be required since User Code makes use of a nesting store in which all the required values of K, Y and Z would be calculated and stored without having access to and from the main store which would use up considerably more time.

Tables 18 and 19 have been drawn up in order to compare the vapour pressure values and the derivatives of the various equations.

Mention has already been made of the first three equations which leaves only the 1966 and 1967 K functions and equation (137) to be discussed. The two former have both been constrained to give p = 221.2 bar exactly and in doing this have lowered the pressure at 374 ^{o}C to the limit of the tolerance. The only other point of significance in these two tables is that the value of the derivative at the critical point for the 1967 K function is zero due to the form of the constraint.

It is now possible to draw conclusions about all the equations examined. Firstly any of the above equations would provide an adequate representation of the vapour pressure. Secondly if the prime criterion for the choice of equation is speed, (where the derivative is not required) then the obvious equation to use is the 1967 K function. Thirdly, if the most important criterion is accuracy and consistency then equation (137) would be the obvious choice since it is the most accurate of the three and since a supplementary equation is also supplied.

5.4. Liquid volume

It was again found convenient to use the entries in the NEL Steam Tables as input data since they are in exact agreement with the IST values which are derived directly from the NBS table, which in turn is based on the measurements of Chappuis (72), Thiessen (73) and Smith and Keyes (27). The experimenters at the NBS found that the observations of Smith and Keyes

were not in agreement with their own calorimetric observations above a temperature of 330 °C. In order to confirm the reliability of their own experimental measurements Osborne, Stimson and Ginnings carried out special volumetric observations in the neighbourhood of 370 °C and consequently computed liquid volume values above 330 °C from their own calorimetric observations.

From the above history it is to be expected that liquid volume will be one of the most accurately represented properties due to the large number of experimental values which were available for its original correlations at the NBS and at MIT. For this reason and due to the fact that these values should provide good agreement and continuity with the other observations of the NBS it was decided that it was necessary to provide a liquid volume equation.

5.4.1. Liquid volume equation

As usual when trying to find the most suitable form of an equation rough plots were drawn up.

From these it was seen that v_f fitted as a function of temperature produced a line with a more severe curve than if the inverse of v_f were plotted. It thus appeared likely that the best form of the dependent variable would be $1/v_f$. As the graphs were not of any great assistance apart from this one factor they have not been included. The following four forms of equation were tried and the results can be seen in Table 20 for different values of k. In each case the best fit required only 11 coefficients.

$$v_f = f\{(t)^k\} \qquad (x)$$

$$v_f = f\{(\tfrac{1}{T})^k\} \qquad (xi)$$

$$1/v_f = f\{(1 - t/tc)^k\} \qquad (xii)$$

$$1/v_f = f\{(Tc/T - 1)^k\} \qquad (xiii).$$

In accord with the results of earlier equations the best value of k was found to be 0.4 using form (xii). Thus the form of the equation in dimensionless

form is

$$\frac{1}{\chi} = \sum_{r=0}^{10}{}' c_r T_r(z) \qquad \ldots\ldots(139)$$

where $z = 1 - 2(1 - t/t_{cl})^{0.4}$.

After all the saturation equations had been correlated it was discovered that the critical values of different properties calculated from the liquid and vapour phases did not agree. Thus it was found necessary to alter slightly the critical values given by the liquid volume and the vapour enthalpy equations. A full description and survey of the critical properties is given in section 5.8. It will suffice for the moment to say that the liquid volume equation was weighted slightly to give a value for v_c of 3.15 cm^3/g.

Fig 14 shows the deviations of the NBS recommended values from those of equation (139). It was found appropriate to include values derived from the recent data of Kell and Whalley (74) which extend over the temperature range 0 °C to 150 °C. In this case Whalley's general correlating equation was used in conjunction with the vapour pressure equation (137) given here. The results, as can be seen from fig 14, are in good agreement with equation (139).

Table 21 demonstrates how well the equation values agree with the 1963 IST values and that nowhere is more than 60% of the tolerance used.

5.5 Correlation of the NBS α values

The α observations are the most important of the NBS calorimetric observations and may be considered second only to the pressure-temperature relation for the saturation line which is fundamental. In deriving the saturation properties it seemed preferable to follow the procedure laid down by Osborne. Accordingly it was decided to refit the α measurements over the whole temperature range replacing the two NBS equations with a single equation.

However before proceeding with the correlation it was necessary to alter the units, int. J, in which α was expressed and convert them to abs. J or J using the relation,

1 int. J (NBS) ≡ 1.000165 J.

Also note had to be made of the fact that the datum state has been changed since Osborne devised the α equation. This however does not affect the value of α itself, but only the relations in which it is used.

Fitting was carried out using an equation of the form

$$\frac{\alpha}{p_{cl}\, v_{cl}} = \sum_{r=0}^{11}{}' d_r T_r(Q) \qquad \ldots\ldots(140)$$

where $Q = (2(1/\theta - C)^k - d_{12})/d_{13}$

with the results shown in Table 22. In this equation the important deviation is the maximum percentage deviation since this occurs at the triple point. Using this criterion as the final judge the constants were given the values C = 0.99 and k = 0.5.

As with the liquid volume equation the critical value of α had to be slightly modified by weighting.

A deviation plot of $(\alpha_{EQN} - \alpha_{OSG})/\alpha_{OSG}$ is included as fig 15 from which it can be seen that above 20 °C the maximum deviation is less than 10 p.p.m. (or 0.001%). For lower temperatures than this a larger deviation is expected since as $t \to 0$, $\alpha \to 0$ and so at t = 0 °C the deviation will be infinite. Since the actual observations of α were in reality observations of $\frac{d\alpha}{dT}$, a comparison is made in fig 16 of the deviation in $\frac{d\alpha}{dT}$ between the two equations and this plot also reflects the accuracy of the new equation.

5.5.1 Conversion of α to new datum state

The NBS α values were calculated using the old datum state which was defined by the following relation:

at t = 0 °C, h = 0 and s = 0.

However this was altered by the 5th ICPS in 1956 to give the new datum state based on the triple point. It is

at t = 0.01 °C, u = 0 and s = 0.

In order to correct α to the triple point datum a constant value, which will now be calculated, must be added thus

$$\alpha_{NEW} = \alpha_{EQN} + K.$$

The constant K is calculated as follows:

$$h = u + pv \quad \text{by definition}$$

and so at t = 0.01 then

$$h_t = 0 + p_t v_t$$

but h_t is calculated using the calorimetric quantities α and β'

using the formula $\quad h_t = \alpha_t + \beta_t'$

$$\text{where} \quad \beta_t' = v_t \left(T\frac{dp}{dT}\right)_t$$

hence in order to obtain h_t correctly it is necessary to modify α_t.

$$\text{so} \quad \alpha_t = h_t - \beta_t'$$

$$= p_t v_t - v_t \left(T\frac{dp}{dT}\right)_t$$

$$= v_t \left(p_t - \left(T\frac{dp}{dT}\right)_t\right)$$

$$= 1.00018\ (0.006112 - 0.012121)$$

$$= -0.0060101.$$

Hence α_{NEW} must be -0.0060101

but $\alpha_{EQN} = 0.0415834$

$$\therefore \quad K = \alpha_{NEW} - \alpha_{EQN} = -0.0060101 - 0.0415834$$

$$= -0.0475935.$$

Hence in all the thermodynamic and calorimetric equations α must be replaced by $\alpha + K$,

e.g. $h_f = \alpha + \beta'$ must be written $h_f = (\alpha + K) + \beta'$.

5.6 Calculation of the remaining liquid properties

It is now possible to calculate the other liquid properties using only the equations already obtained and the relations expressed in section 4.3.3. The first of theseis the other liquid calorimetric property, β', which is

calculated using relation (102)

$$\beta' = v_f T\frac{dp}{dT} .$$

The values obtained are compared with those calculated by Osborne, Stimson and Ginnings in Table 23. The resulting agreement to less than 0.2 % for temperatures less than 374 ^{o}C is more than adequate and even although the difference is approximately 1% round the critical this is much less than the uncertainty.

The next property to be obtained is h_f by using relation (104)

$$h_f = (\alpha + K) + \beta' .$$

The value of K was calculated in the previous section and so it only remains to compare the results with the IST as has been done in Table 24. The accuracy of this property is excellent as even 50% of the tolerance is reached only once but in general any disagreement in the values is due mainly to rounding off.

The last property which can be obtained is liquid entropy, s_f, which is calculated from the equation (108)

$$s_f = \left[h_f/T\right]_{T_t}^{T} + \int_{T_t}^{T} \frac{\alpha + K}{T^2}\, dT.$$

This expression appears to be very complicated especially the integral. However there are two possible ways of dealing with it. The first is by a numerical integration method like Simpson's Rule but this is a rather slow and untidy process whereas an analytical solution should be much faster and neater. The only possible method of tackling it appeared to be by transformation.

First of all the α equation may be written

$$\alpha = p_{cl} v_{cl} \sum_{r=0}^{11}{}' d_r T_r(Q)$$

$$\text{where } Q = (2(\frac{1}{\theta} - 0.99)^{0.5} - d_{12})/d_{13}.$$

Hence

$$dQ = \frac{2}{d_{13}} \times 0.5\ (\frac{1}{\theta} - 0.99)^{-0.5}(\frac{T_c}{T^2})\ dT$$

$$= -\frac{T_c}{d_{13}} \cdot \frac{2}{(d_{13}Q+d_{12})} \cdot \frac{dT}{T^2}$$

$$\therefore \frac{dT}{T^2} = - \frac{d_{13}\ (d_{13}\ Q + d_{12})}{2T_c}\ dQ$$

Now $\int_{T_t}^{T} \frac{\alpha+K}{T^2}\ dT = \int_{T_t}^{T} \frac{\alpha}{T^2}\ dT + \int_{T_t}^{T} \frac{K}{T^2}\ dT$

where $\int \frac{\alpha}{T^2}\ dT = - \frac{d_{13}}{2T_c} \int \alpha (d_{13}Q + d_{12})dQ$

$$= - \frac{d_{13}}{2T_c} \left[d_{13} \int \alpha\ Q\ dQ + d_{12} \int \alpha\ dQ\right]$$

$$= - \frac{d_{13}}{2T_c} \left[d_{13}(Q \int \alpha\ dQ - \int\int \alpha\ dQdQ) + d_{12} \int \alpha\ dQ\right]$$

$$= - \frac{d_{13}}{2T_c} \left[(d_{13}\ Q + d_{12}) \int \alpha\ dQ - d_{13} \int\int \alpha\ dQdQ\right]$$

Hence $$\int_{T_t}^{T} \frac{\alpha}{T^2} dT = - \frac{d_{13}}{2T_c} \left[(d_{13}\ Q + d_{12}) \int_{Q_t}^{Q} \alpha\ dQ - d_{13} \int_{Q_t}^{Q} \int_{Q_t}^{Q} \alpha\ dQdQ\right] \qquad .....(141)$$

where Q_t is the value of Q at the triple point.

Now $\int_{T_t}^{T} \frac{K}{T^2}\ dT = K \frac{T - T_t}{T.T_t}$

This only leaves the problem of integrating the α equation which can be achieved by writing the integral as a Chebyshev polynomial thus:

$$\int_{Q_t}^{Q} \alpha\ dQ = p_c\ v_c \sum_{r=0}^{12}{}' D_r\ T_r(Q)$$

using the integration formula (75) to obtain the values $D_1, D_2, \ldots D_{12}$, the coefficient D_o being determined by the lower limit of integration, Q_t, as follows:

$$D_o = - 2 \sum_{r=1}^{12} D_r\ T_r\ (Q)$$

$\int_{Q_t}^{Q} \int_{Q_t}^{Q} \alpha\ dQ\ dQ$ is calculated in identical fashion.

Hence the liquid entropy was calculated using this equation

$$s_f = \left[{}^{h}/_{T}\right]_{T_t}^{T} - \frac{d_{13}}{2T_c}\left[(d_{13}\,Q + d_{12})\int\alpha\,dQ - d_{13}\int\int\alpha\,dQ\,dQ\right] + K\left(\frac{T-T_t}{TT_t}\right) \quad .....(142)$$

The values obtained from this equation are compared with those in the NEL Tables (Table 25) which in turn were taken from the NBS values. The agreement is yet again almost exact below 370 ^{o}C and provides as good a fit as the liquid entropy equation (133) over this range. As expected towards the critical point the agreement is not quite so accurate due to the readjustment made to the critical point properties.

There are other properties (u_f, g_f, f_f) which could now be calculated also but as they are normally neither tabulated nor measured it is pointless to calculate them at this stage. They are all however evaluated in Appendix IV.

The equations described to date have been shown to provide an accurate representation of all the liquid properties. The next stage is to find a saturated vapour equation.

5.7 Saturated vapour properties

Now all the vapour properties can be deduced if γ is now expressed as a function of temperature. This in fact was the procedure used by the NBS in generating their table of properties and was the only valid procedure since γ was an observed property. However, it has proved more convenient to fit h_g as a function of temperature and to compare the calculated values of γ with the observed values of the NBS. This course was dictated by the fact that a complete table of h_g values was ready to hand in the NEL Tables, whereas it would be necessary to generate values of γ from the NBS data. Moreover, in view of further work on equations of state planned by the author it was recognised that it would be more convenient to have h_g as a function of T rather than γ or h_{fg}. It is to be appreciated that only one of these properties need be defined since the other two can then be evaluated.

5.7.1 Vapour enthalpy equation

Fitting was carried out for an equation of the form

$$h_g = f\{(\frac{T_c}{T} - 1)^k\}$$

using different values of k (Table 26). A value for k of 0.4 proved to be more than sufficient as the maximum percentage deviation is only 0.015 % which is within the round-off error of the original data as it is given only to four significant figures. This is demonstrated very forcibly in Table 27 as only at the critical point is the difference between the equation and IST values greater than 1 J/g. As with the previous equations the critical value had to be modified slightly and a final equation of the following form was obtained

$$\frac{1}{e} = \sum_{r=0}^{10}{}' e_r T_r(\omega) \qquad .....(143)$$

where $\omega = 1 - e_{11}(\frac{1}{\theta} - 1)^{0.4}$

and $\frac{1}{e} = \frac{p_{cl} v_{cl}}{h_g}$.

If fig 5 is examined closely then it is seen that there is a maximum on the vapour enthalpy curve. It is of interest to discover at what temperature this occurs and so the temperature which satisfies the condition $\frac{dh_g}{dT} = 0$ for the above equation was evaluated. It was found to be satisfied by $t = 234.615251\ ^{o}C$.

5.7.2 Other vapour properties

It is now possible to evaluate γ the last of the NBS calorimetric properties by using the relation

$$\gamma = h_g - \alpha \ .$$

The values obtained are compared in fig 17 with the smoothed NBS values and the values re-correlated by Bridgeman and Aldrich (75) above 300 ^{o}C, both of which were based on the NBS measurements. The agreement obtained is

very good and the disagreement increases with increasing temperature which is how the experimental accuracy behaves.

The next property to be calculated is vapour volume and this is done with the relation

$$v_g = {}^{\gamma}/_{T}\frac{dp}{dT}$$

and the results are compared with the IST values in Table 28. The biggest discrepancy between the values when compared with the tolerance occurs at 374 ^{o}C and only takes up 25% of the tolerance.

The only quantity that remains to be calculated is the vapour entropy s_g which is calculated from

$$s_g = s_f + {}^{h_{fg}}/_{T} \quad .$$

The results are tabulated and compared with the NEL values in Table 29 with almost identical accuracy to the liquid entropy comparison.

Thus all the most important saturated properties, both liquid and vapour, have been calculated and compared either with the 1963 IST or the NBS values as presented in the NEL Tables. In every case the deviations are well within the tolerances or possible experimental errors in the data.

5.8 Critical point properties

Apart from the low temperature vapour pressures which may be in error, by a small amount the only other region where there is some doubt is around the critical point. It is inevitable that a fairly large uncertainty must be associated with the values of the properties at the critical point.

In order to demonstrate this uncertainty Table 30 has been drawn up with the successive experimental values obtained during the past 60 years. It is certainly necessary, as suggested by Juza (45), to carry out further experimental and theoretical work, such that the uncertainties on the various critical propeties may be reduced. This necessity is emphasised very strongly by the latest measurements carried out earlier this year by Blank (86) at Erlangen. The values he obtained are considerably different

from those accepted by the 1963 IST and are in fact well outwith the tolerances. Moreover even if his estimated error is included his values are still outwith the 1963 IST tolerances.

It is interesting to compare the values of p obtained from the vapour pressure equations for the various experimental values of t (Table 31). The different equations provide fairly close agreement with each other and not unreasonable agreement with experimental values of p with the exception of Bridgeman and Aldrich's value based on the recorrelation of the NBS data.

Table 32 compares the derivatives $(T\frac{dp}{dT})$ of equation (137) above 370 °C with those of the NBS (1932) (87), Egerton and Callander (88), Keyes (MIT) (89), NBS (1939) (22), Bridgeman and Aldrich (62) and the 1966 IFC K function. It is interesting to note that the 1966 K function gives higher values than the others. It is also interesting to note that the average value, excluding that derived from the K function is close to the predicted values given by equation (137) and by Bridgeman and Aldrich. The value of $(T\frac{dp}{dT})_c$ would appear to be close to 172 J/cm^3.

The value of the critical volume would certainly appear to be less than the 1963 IST value of 3.17 cm^3/g. In addition to the values given in Table 30, if the method of rectilinear diameters is used then a value of approximately 3.11 cm^3/g is obtained.

A very interesting paper (90) on the critical region was published in 1966 by Bridgeman, in which he discussed the values of the critical point derivatives for various properties. These values, which are mostly $\pm \infty$, are given in Table 33 together with the values obtained from the saturation equations. Due to the form of the variables chosen for the equations all the critical derivatives turn out to be in agreement with the theoretical values.

Another important point which appears in this paper is the recommendation of a temperature variable of the form $\left[3(1 - \frac{T}{T_c})\right]^{1/3}$ in the correlation of data on saturated fluid properties. This is very interesting as the function

used in most of the saturation equations and arrived at independently is $(\frac{T_c}{T} - 1)^k$ where $k = 0.4$. Both these functions are almost identical and provide fairly good agreement between the powers. Hence it would appear, as suggested by Bridgeman, that this type of function should prove very useful in analytical studies and correlation of properties in the critical region.

5.9 Thermodynamic consistency

It is now possible to examine the equations as to how closely they maintain thermodynamic consistency. The agreement should be excellent since only the minimum number of equations are used and the thermodynamic relations are used to calculate the remaining properties. However there are two good criteria which can be used to show conclusively that the saturation equations do not contain any inconsistencies of a thermodynamic nature. These two criteria will now be described.

The first is that the saturated liquid and vapour values of Gibb's function should be identical i.e. $g_f = g_g$. Table 34 has been drawn up to show the difference between these values. In all cases the deviation does not exceed $8_{10}-9$ J/g which, above 120 °C, represents 12 significant figures or the limits of accuracy on the computer. In fact the deviations in this region amount purely to round-off error. In fact the most significant deviation is at 0 °C where it is $7.6_{10}-9$ J/g (or $7.6_{10}-8$%).

The second is the use of the Clausius Clapeyron relation, which may be written

$$T \frac{dp}{dT} = T \frac{s_{fg}}{v_{fg}} \quad .$$

These results are also included in Table 34 and again successfully demonstrate the accuracy of the equations and their compatibility. The largest deviation occurs at the critical point ($= 5.04_{10}-7$ J) and shows that the critical values are not quite as consistent as the other entries. This is not particularly surprising as these values had to be modified slightly in order to obtain

agreement between the liquid and vapour values of the same property at the critical point.

However if the properties such as c_p, c_v etc are to be calculated it is necessary to obtain one of the partial derivatives $(\frac{\partial v}{\partial p})_T$ or $(\frac{\partial v}{\partial T})_p$. These values can only be calculated from an equation of state whose variables are p, v and T and the introduction of these quantities will necessarily raise the question of thermodynamic consistency. However as these properties can be calculated only by using other derivatives this whole subject will be dealt with in Appendix IV.

CHAPTER 6

CHARACTERISTIC EQUATIONS

6.1 Introduction

Before carrying out any surface fitting of the properties of water and steam it was necessary to decide firstly which variables should be used and secondly what data was required and for which regions. Thus it was necessary to examine the above points before carrying out any correlations, although it was possible to write and test the necessary computer programs which would be required at a later stage.

6.1.1 Choice of variables

In an address to the Sixth International Conference on the Properties of Steam, New York 1963, R. W. Bain suggested that it might be possible to cover the entire liquid and vapour regions with a single equation of the form $h = h(p,s)$ - other forms are $p = p(h,s)$ and $s = s(h,p)$. This is one of four canonical equations

$$u = u(s,v) \quad \text{(144)}$$

$$f = f(v,T) \quad \text{(145)}$$

$$g = g(T,p) \quad \text{(146)}$$

$$\text{and } h = h(p,s) \quad \text{(147)}$$

which possess a number of advantages over those in which the various properties (h, v, s etc.) are expressed as functions of p and T. If $p = p(v, T)$ (148) not only is it unlikely that a single equation can cover both the liquid and vapour phases but additional information has to be supplied in order that energy quantities may be calculated. This is usually expressed as $c_p^{o} = f(T)$ (149).

Formulations, comprising equations (148) and (149) for example, involve both integration and differentiation in computing the usual properties, whereas any one of the canonical equations (144) to (147) defines all thermodynamic properties using only the quantities themselves and their derivatives. The

derivation of the various thermodynamic properties from the four canonical equations was demonstrated by Bain and Le Fevre (41) in a paper from which the entries in Table 35 have been taken. Columns (1) and (2) of this table give the quantities appropriate to the canonical equations (147) and (145) and column (3) refers to equation (148), which is not a canonical form and for which it can be seen that both integration and differentiation are required.

In addition to the computative advantages of the canonical equations derivative quantities across the saturation line are smooth and all quantities are continuous. The absence of gross discontinuities such as are exhibited by an equation of the form $p = p(v,T)$ is a further factor in favour of the surface $h = h(p,s)$, which is represented in fig 18. This particular type of equation seems to have been advanced in the first instance by Holmes and Hollitch (37) who covered the field of industrial interest with a series of equations for compressed water and steam. Juza (91) has also presented equations of this type specifically for industrial calculations but no attempt to provide a single equation, as suggested by Bain, has yet succeeded. Haywood and Bott at the instigation of the UK Committee on the Properties of Steam (ERA Research Advisory Committee 2B as it was then termed) made a preliminary investigation which was subsequently followed up by McLeod at the National Engineering Laboratory. Taking the form of the surface as $s = s(p,h)$ _____(150) and using constraints McLeod was unable to obtain a surface from which satisfactory properties could be derived. As a contribution to the UK effort the saturation properties were respecified in terms of equations suitable for computers (reference (92), see Appendix V) before moving on to the problem of the h-p-s surface. It is this latter work which is described here and which is believed to supply a valuable clue to any future fitting of this or similar thermodynamic surfaces.

Once it was decided to work on the h-p-s surface the obvious choice of independent variables was pressure and entropy as in equation (147) since McLeod had already used the inverse form in equation (150).

6.1.2 Choice of input data

It is not possible to use experimental data as none exists for entropy and very little is available for enthalpy. Hence the input data must be obtained either from tables or from equations of state. It was thought that the most recent tables, which were the NEL Steam Tables, would be quite adequate in the first place for providing some initial correlations. If they did not give the necessary accuracy then the input data would have to be calculated from one of the computer formulations which was available.

It was necessary to consider the various formulations which could then be used if the NEL Table values proved inadequate. There were three possibilities. Of these the BRD and Japanese formulation were fairly similar in form but they had large inter-regional discontinuities. The third had been prepared by Juza of the CSSR and provided greater accuracy and smaller discontinuities than either of the other two. (These discontinuities are tabulated in Appendix VI.) Its major drawback was the increased number of constants that it contained.

There was one further equation, provided by Whalley and based on his own p-v-T measurements, which was valid for compressed water in the temperature range 0 ^{o}C to 150 ^{o}C. The data on which it was based was more accurate than previous experimental work and it was felt that if this region could not be adequately fitted then the proposed method could not possibly be applied to water substance.

This equation had already been used by Leong and the author in preparing a note for the 2nd IFC on the derivation of some of the less used properties, and in particular the speed of sound. From this work it was confirmed that the equation was easy to use and that its derived quantities were in excellent agreement with experimental results.

6.1.3 Form of equation

Since the method of surface fitting was decided on and described in Chapter 3 it is only necessary to show how it was applied. The variables

used were h-p-s and since the data in the NEL Tables was provided for isobars (i.e. lines of constant p) then the simplest approach was to fit h = h(s), as shown in equation (151),

$$h = \sum_{i=0}^{n}{}' C_i T_i(X) \qquad \text{.....(151)}$$

where $X = (2s-CA)/CB$.

Then the coefficients were fitted as a function of pressure as in equation (152)

$$C_i = \sum_{j=0}^{m}{}' D_{i,j}\, T_j(Y) \qquad \text{.....(152)}$$

where $Y = (2p-DA)/DB$.

Hence the final form of the equation may be written

$$h = \sum_{i=0}^{n}{}' \sum_{j=0}^{m}{}' D_{ij}\, T_i(X) T_j(Y) \qquad \text{.....(153)}$$

6.2 Input data from NEL Tables

Following on from the decision to use the NEL Steam Tables for input data, it was necessary to decide which region - high temperature, compressed water, superheated steam, etc. should be fitted. It was felt that rather than try to fit the entire surface with one equation immediately, smaller regions where the properties were most regular should be correlated first, omitting the more difficult and less well-defined regions, such as the critical region, until the method had been proved. Thus it could be seen on examining fig 10 that the compressed water region and the high pressure region had the most regularly spaced isobars and isotherms. Based on this observation it was decided to attempt to correlate the high pressure region first since it would provide a guide to the likelihood of fitting the surface with a single equation. The results of this investigation will now be discussed.

6.2.1 Curve-fitting along isobars

The first step in attempting to correlate the high pressure region was to fit h = h(s) along various isobars and to find how many coefficients were

necessary for the temperature range 0 °C to 800 °C. After this had been done for isobars between 250 bar and 1000 bar it was found that 10 coefficients appeared to provide the best fit although at the lower pressures of 300 and 250 bars 11 coefficients improved the fit. These results, given in Table 36 for equation (151), show that the maximum deviations, 0.83 J/g at 1000 bar, 0.88 J/g at 400 bar and 1.73 J/g at 250 bar are all well within the IST tolerances. It would appear that more coefficients may be required at the lower pressures although this question should be answered when this region is finally fitted.

The second step is to examine a plot (fig 19) of the coefficients, C_i, against pressure in order to see if a smooth curve is produced. If this is the case then there should be very little difficulty in fitting equation (152). When fig 19 is examined it is obvious that the plots of the coefficients C_o and C_1, are almost straight lines, both of them having a very slight concavity. It would appear from these results that there is a reasonable chance of an equation of this nature providing a good fit to the data, certainly as far as enthalpy is concerned.

The next step is to check that the derivatives obtained by the equations for the isobars are accurate. In other words since $T = (\frac{\partial h}{\partial s})_p$ an evaluation of $\frac{dh}{ds}$ from equation (151) for any particular isobar, say 700 bar, should show how well the derivatives will be represented in any equation. The results of this examination are given in Table 37 and it is interesting to note that the maximum deviations in t occur at the extremities 0 °C and 800 °C. Ignoring these values the largest percentage deviation, $\frac{\Delta t}{T} \times 100\%$, is approximately 0.1%. There is no difficulty in constraining the end points of the isobars i.e. at t = 0 °C and at t = 800 °C to give corrected temperatures. In fact this has been done in Table 38 and it can be seen that when h_o and T_o are constrained then the standard deviation on temperature is considerably reduced. Unfortunately when h_{800} and T_{800} are constrained the improvement is not nearly so great. This may be caused by inaccurate values of enthalpy at the higher temperatures.

It is also possible to examine c_p in a similar manner since $c_p = (\frac{\partial h}{\partial s})_p / (\frac{\partial^2 h}{\partial s^2})_p$ but as this property is not tabulated in the 1963 IST it is very difficult to put a tolerance on the experimental values or tables based on them. However, based on the isobaric equations it was noticed that the values of c_p had two maxima (at ~ 50 °C and ~ 490 °C for 700 bar) and a minimum (at ~ 90 °C for 700 bar). These phenomena are not reflected in the experimental values, where a maximum is to be found only at ~ 490 °C, and would appear to be caused by errors in the original enthalpy or entropy data.

In order to try and improve the values of T and c_p obtained from the equations it was decided to introduce the derivative T into the curve fitting routine as was described in 3.2.7. This was done by minimising $\Sigma(h - h_{EQN})^2 + \lambda\Sigma(T - T_{EQN})^2$ and allowing the factor λ to adopt various values.

Table 39 has been drawn up to show how variations in λ affect the correlation for a pressure of 700 bar. It can be seen that as λ is increased the standard deviations on both enthalpy and temperature increase also. This effect was quite unexpected but on a reappraisal of the results it is seen that the largest deviations on temperature have been reduced although to the detriment of the other deviations. This has been shown in Table 39 by tabulating the deviations of the other correlations for the temperatures at which the largest deviations occur, and thus adequately demonstrates the effects of this technique. Unfortunately it is not of much assistance as the overall amount by which the fit is improved is negligible. An approach which is likely to be more successful is the addition of extra data points. By this means the derivatives obtained should be much smoother, and the end points can be dealt with by using constraints as has already been demonstrated. The problem was tackled in this manner in all later work and was found to be successful so derivatives were never again used in the correlating procedure.

6.2.2 Surface fitting

The final step is to carry out the fitting of equation (152) for various values of m and to examine the results obtained. This would have two effects:

firstly it would provide a check on the computer programme and secondly it would give a comparison of the accuracy obtained by fitting the isobars and the accuracy of the full equation.

The region to be fitted was the high pressure range with the data made up from the intervals 700 bar by 20 bar to 1000 bar and 0 °C by 10 deg C to 800 °C. Using the results of the curve-fitting it had appeared that the optimum value of n was 9 (i.e. 10 coefficients) and so correlations were undertaken for various values of m as shown in Table 40. The different fits were compared with the original data and the standard deviations of the properties enthalpy, temperature and volume are given in this table for different pressures. The best fit appeared to be the one with m = 3 although some of the others were almost as good. In order to confirm that n = 9 was the best, some more fits were carried out in which n was varied but they only served to confirm that the equation with n = 9 and $_m$ = 3 provided the best fit to the data.

Since Haywood and Bott had recommended the use of ln p instead of p the equation was refitted with this modification but there was no improvement in the resulting correlation. Thus at this stage attention was concentrated solely on the h-s-p formulation.

A comparison of the equation values from the best fit was made with the 1963 IST values and tolerances in Table 41 and the following conclusions may be reached. Firstly that the equation gives enthalpy values which are everywhere within the tolerance and secondly that many of the volume values lie considerably outside the tolerances. It is also interesting to note that the maximum deviations Δh and Δt obtained from the surface fitting procedure are only marginally larger than those obtained from the curve fitting. The maximum percentage deviations of the temperature are also too large because if the equation was entered with p and t and h was calculated then there would be an error on h of the order of 0.5% which in some cases is larger than the tolerance.

The final point worth noting from Tables 40 and 41, and one which is not

unexpected, is that the volume values of the isobars bounding the equation (i.e. 700 and 1000 bar) are much more poorly represented by the equation than those on the middle of the range of pressure.

In order to check that all these results were not caused by some factor which only occurred at high pressures a few isobars were fitted for compressed water at low pressures. The coefficients of these fits when plotted were not nearly as smooth as those shown in fig 19 and only served to emphasise the unsuitability of the NEL Tables.

From all the information which has now been obtained it is quite obvious that the NEL Tables cannot be used as input data in the correlation of new equations. This decision may be explained by the following factors:

(a) There are rounding and smoothing errors in the data which produce in the course of any correlation a considerable amount of unwanted 'noise' and thus reduce the accuracy of the curve-fitting procedure.

(b) There are systematic errors in the data which introduce considerable errors into the derivatives of the new correlation.

(c) There are not enough entries in the Tables to help to overcome either of the above problems i.e. p and t require to be tabulated at closer intervals.

The problem which is mentioned in (a) was forecast by Haywood and Bott in their 'suggestions for future work'. Their idea for overcoming this problem was to use only experimental data as input and thus avoid the effects of smoothing. This method would necessitate all the suitable experimental data being sorted and evaluated in order to discover how reliable and accurate it was and this would take a considerable time.

It would thus appear that the only suitable method of obtaining input data would be to calculate the properties from one of the available computer formulations already mentioned.

6.3 Input data from Whalley's equation

It has now been conclusively demonstrated that as a source of input data,

steam tables neither have enough entries nor the required accuracy for use in correlating equations of state. This source of data would be adequate as long as a fit was only required for the dependant variable and no derived quantities were needed since it is in the course of differentiation that the gross inaccuracies become so obvious. Thus it was decided to correlate the compressed water region using Whalley's equation after which Jura's formulation could be used for correlating the entire surface of water and steam.

This equation was obtained from the experimental data by the method of 'least-squares' and is a simple polynomial of the form

$$\frac{v}{v_A} = 1 + \sum_{i=0}^{5} \sum_{j=1}^{3} W_{ij} t^i (p-p_A)^j \qquad \text{.....(154).}$$

Equation (154) cannot be used without certain additional information relating to v_A and the saturated liquid values. The necessary saturated liquid values were obtained from the equations in Chapter 5 and values of v_A were derived from an expression described in Appendix VII and published by Bridgman (93).

In this latter publication the volume measurements of Kell and Whalley are compared with those of Amagat (94), Smith and Keyes (27), Kennedy, Knight and Holser (95) and Vukalovich (96). There is little doubt that the data of Kell and Whalley enable the best possible evaluation of the thermodynamic properties of compressed water to be made and the next stage of the work was to repeat the earlier surface-fitting. Since the volumes were given to six significant figures it was decided to calculate all the input data to six significant figures also and to have as many isobars as isotherms. The values of enthalpy and entropy at intervals of 1 deg C along the isobars were evaluated from equation (154) using the relationships in column 3 of Table 35.

6.3.1 Curve fitting along isobars

Once the input data had been evaluated curve fitting was carried out for different pressures. The improvement in accuracy obtained is very noticeable since the deviations and standard deviations on both enthalpy and

temperature are smaller than those from the NEL Table correlations by a factor of between 20 and 100. This is shown very clearly if Table 42 and 36 are compared. In order to emphasise the difference between using tables and correlations as a source of input data Table 43 was drawn up. This shows the differences Δh and Δt for the 1000 bar correlation and since the maximum value of Δt is less than 0.1 deg C (0.036%) the chance of finding an accurate equation looked very good. This is because if the equation was interpolated for a particular value of temperature then the corresponding value of enthalpy would be altered by less than 0.036%. In order to discover if the deviations of the equation from the 1963 IST values were greater than the tolerances, it was possible to draw up the following bands of tolerance for enthalpy:

$$0.01 \text{ J/g} \geq \text{Tolerance on } h \geq 1.2 \text{ J/g}$$

$$0.47\ \% \geq \%\ \text{Tolerance on } h \geq 17\%.$$

Hence the percentage correction to h based on the difference Δt lies well within the band of percentage tolerance.

It may possibly be argued that the comparisons between the correlations based on the NEL Tables and those of Whalley's equation are not valid since they cover different temperature ranges. It was felt though that this was quite legimate as it is the best fit that is being compared which in the former required 10 coefficients and in the latter only 5 coefficients and thus it was possible to draw comparisons between them.

Finally the coefficients were examined graphically and as they provided a smooth plot for pressures between 1 and 1000 bar it was with confidence that the surface fitting process was tackled.

6.3.2 Surface fitting

Surface fitting was now carried out using 20, 100, 160, 200 and 300 isobars in order to discover whether the number of isobars was critical. From the results for different numbers of coefficients it was found that about 200 isobars

gave the best fit. Thus for the correlations to be carried out the following isobars were used; 1 bar by 1 to 100 bar by 5 to 200 bar by 10 to 1000 bar. For n = 4, m was given different values as shown on Table 44. By comparing the standard and maximum deviations for the isobars 1000, 600, 200, 100, 50 and 10 bars, it was concluded that a value of m = 3 gave the optimum results.

By using the experience gained in working with the NEL data it was then possible to estimate whether the equation lay within the IST tolerances. First of all an examination of the maximum percentage deviation on both h and t confirmed that the minimum percentage tolerance on h of 0.47% was not exceeded. The bands of tolerance on v are given by

$$0.0001 \text{ cm}^3/\text{g} \leq \text{Tolerance on v} \leq 0.0005 \text{ cm}^3/\text{g}$$

$$0.01\ \% \leq \%\ \text{Tolerance on v} \leq 0.048\%.$$

Now both the maximum deviation and the maximum percentage deviation exceed the maximum tolerances and so without examining every entry it can be deduced that the equation does not satisfy the criteria laid down in the 1963 IST.

Before carrying out any improvements to the equation it is necessary to find out how many points lie outwith the tolerances, since if there are only a few a simple alteration to the equation might suffice. It was found that over the whole region the new equation gave values within the IST tolerance except for volumes along the 150 ^{o}C isotherm at pressures below 150 bar and for enthalpy at 0 ^{o}C and 1 bar.

There were only two possible methods, either weighting or constraining the fit, which could be used to overcome this difficulty. Since there were only a very few points which lay outside the tolerances it was decided to refit using the weighting procedure mentioned in 3.3.2. It was hoped that this would prove successful and thus avoid the complication of introducing constraints into the equation.

It is impossible to show any of the results and so all that will be said is that weighting was carried out on the isobars for the low pressures by a 'trial and error' process until a suitable fit was obtained. The coefficients

for this final form of the equation are tabulated in Appendix VIII. The equation is written

$$h = \sum_{i=0}^{4}{}' \sum_{j=0}^{3}{}' D_{ij} T_i(X) T_j(Y) \qquad .....(155)$$

where $X = (2s - 11.99)/12.01$

and $Y = (2p - 1000)/1000.$

This final equation meets the criteria laid down by the 1963 IST. At all the skeleton table points the values of enthalpy lie within the tolerances while the values of volume also lie within the tolerance with the exception of the 150 °C isotherm from p = 25 bar to p = 125 bar where the values take up all the tolerance. This is demonstrated in Table 45. The saturation line provides a boundary to the equation from 100 °C to 150 °C and a comparison with the IST saturated liquid values from 100 °C down to 0 °C so that the possibility of using the equation below 1 bar pressure and so extrapolating its range to the saturation line from 0 °C to 100 °C may be considered. As can be seen from Tables 45 and 46, with the exception of the liquid volume values at 0 °C and 0.01 °C all values are within the prescribed tolerances.

A comparison of the saturation values which may be derived from equation (155) is made in Table 47 with the values previously obtained in Chapter 5. Included are values of c_p, which are calculated from the equation (156),

$$c_{p_f} = \left(\frac{dh}{dT}\right)_f - \left(\frac{dp}{dT}\right)_f \left\{v_f - \left(\frac{\partial v}{\partial T}\right)_p T\right\} \qquad .....(156)$$

where $\left(\frac{\partial v}{\partial T}\right)_p$ is derived from equation (154) and the other quantities from the saturation equations.

6.4 Input data from Juza's formulation

It has been shown that for sufficiently accurate data the method of surface fitting using orthogonal Chebyshev polynomials will provide an excellent interpretation of the actual properties of water. It only remains now to apply

this technique to the entire surface. This process will obviously take a considerable amount of time since there are likely to be considerable difficulties in dealing with the critical region. The first stage is to find out the maximum range of temperature that can be fitted accurately along any isobar. If the compressed water region is tackled first it is necessary to discover whether an equation could be fitted up to 300 °C. It is rather difficult to imagine a simple equation being valid for higher temperatures due to the phenomena present near the critical point.

6.4.1 Curve fitting along isobars

The first stage was to find out what range of temperature would provide the best fit i.e. could an equation be found for compressed water in the range $0 \leq t \leq 400$? This includes the critical region and so it would not be expected that the isobars in the vicinity of the critical isobar would provide nearly as accurate a fit as the others. When fitting of the isobars was carried out at intervals of 2 deg C, it was found that 7 coefficients for the higher pressures gave the best fit, while for a pressure of 250 bar an adequate fit could not be obtained. One point which emerged was that for temperatures above about 320 °C the deviations on h and t increased considerably.

When fitting was repeated for maximum temperatures of 300 °C, 250 °C and 200 °C then 7, 6 and 6 coefficients respectively gave the best fit and since a plot of the coefficients was reasonably smooth it was thought that surface fitting could be carried out for the suggested ranges of temperature with a good chance of success.

Before going on to describe this next stage a few other ranges of temperature were examined. The range 200 °C by 1 deg to 300 °C was fitted very accurately with only 4 coefficients. One conclusion that was drawn from these results was that the smaller the range the smoother the coefficients.

The other range of temperature to be fitted was 300 °C by 2 deg to 800 °C for which 6 coefficients provided the best fit.

These last two pieces of information may be of use at a later stage in the work but based on the results mentioned, the following tentative conclusions were suggested.

range of temperature	maximum number of coefficients
100 deg	4
200 deg	6
300 deg	7

The first results of the surface fitting should either confirm or modify these suggestions and enable curve fitting to be dispensed with completely for the rest of the work.

6.4.2 Surface fitting

Surface fitting was carried out for the range of temperature 0 to 250 ^{o}C at intervals of 2 deg C and for the range of pressure 1 to 1000 bar at intervals of 10 bar. On trying various values of m for n = 5 very poor results were obtained. The cause of this was the fact that although at intervals of 100 bar the coefficients were smooth at intervals of 10 bar they were not. It was found subsequently that the maximum value of n was 4. Furthermore a discontinuity arose for isobars whose pressure was less than the saturation pressure at 250 ^{o}C (i.e. 39.8 bars). This is because 126 points were used in fitting the isobars above 39.8 bar but for all those below, fewer and fewer points were fitted and this radically affected the values of the coefficients and is shown graphically in fig 24. The general nature of this phenomenon was confirmed by fitting equations over different temperature ranges. It may be avoided either by correlating much smaller intervals of temperature and thus increasing considerably the number of equations required or by using the critical isobar as a boundary and dividing the surface into regions as demonstrated in fig 25. The latter method was chosen as it would probably help to keep the final formulation as simple as possible.

In order to ensure that the discontinuities on the boundaries between the

various equations were kept to a minimum, it was decided to fit isobars right down to 50 bar such that the equations A and C would overlap and might not require constraining along the boundary supplied by the critical isobar.

A correlation for region C was then carried out with T_a= 250 ^{o}C, n = 4 and m = 3. On comparing the resulting values with the IST, excellent agreement was obtained with the exception of the 0 ^{o}C isotherm where the tolerance on volume was either equalled (from 500 bar to 1000 bar) or exceeded (under 500 bar). This was a case which called for the use of constraints to reduce the volume values within the tolerance.

Unfortunately the surface fitting programme had been modified to take account only of constraints on h, T or c_p but not on v since it involved a slightly different technique and it proved impossible to include this facility within the time available. A description of the technique was not included in Chapter 3 and the only description of it is given by Clenshaw and Hayes (53).

All that now remains to be done is to make recommendations as to how any future work may be carried out.

6.4.3 Suggestions for the course of future work

The studies made in this chapter make it possible to recommend the course that any future work based on the results of this investigation should take. Since it has been shown that orthogonal Chebyshev polynomials will provide an accurate representation of the h-s-p properties of water substance over suitable ranges it only remains to fit equations to a number of regions such that the property values on the boundaries are identical.

Considering the matter in retrospect, it should be possible to complete the task with the minimum effort and maximum success, assuming that a general programme capable of fitting all kinds of constraints is available, if the following procedure is carried out. Referring to fig 25, region C should be fitted and the values on the isotherm T_o constrained, followed by region D with the isotherm T_a similarly constrained and continuing in this way until the entire surface

for $p > p_c$ has been fitted. Then the regions A and B would be correlated while constraining the saturation line and, if necessary, the critical isobars. It may, in fact, be possible to fit both regions with one equation, as suggested by Bain and by Haywood and Bott, if spurious data were used in the two-phase region.

In this way it is hoped that this particular line of research into the calculation of an h-s-p characteristic equation, which was first suggested by Bain and Le Fevre back in the late 1950's and which has aroused much interest may finally be brought to a successful conclusion.

6.5 Advantages of an h-s-p double-power series over the other types of equation

The argument that follows is quite straightforward but since at different times people have queried the advantages of this method of representation it was decided to include it.

The form of the general equation has already been expressed in equation (153), from which the properties v and T can be obtained by differentiation thus:

$$T = \left(\frac{\partial h}{\partial s}\right)_p = \frac{2}{CB} \sum_{i=0}^{n=1}{}' \sum_{j=0}^{m}{}' F_{i,j} T_i(X) T_j(Y) \quad \text{.....(157)}$$

$$v = \left(\frac{\partial h}{\partial p}\right)_s = \frac{2}{DB} \sum_{i=0}^{n}{}' \sum_{J=0}^{m}{}' G_{i,j} T_i(X) T_j(Y) \quad \text{.....(158)}$$

The coefficients F and G are both calculated from D using the relation (76) (Chapter 3) and can be easily calculated when and if they are required. Moreover only one procedure is needed to calculate h, v and T. This is unusual because in all the other formulations a different routine is required for each property (e.g. 1966, 1967, 1968 IFC and Juza formulations). It is thus possible to state that a formulation using Chebyshev polynomials will result in a much shorter, simpler and faster computer programme than any of the mentioned formulations even if more coefficients are required. The simplest and quickest method of evaluating the double-power series will now be demonstrated and attention

drawn to its advantages.

6.5.1 Evaluation of Chebyshev double-power series

Equation (153) will be used to demonstrate the method. It is possible to write

$$h = \sum_{i=0}^{n}{}' \sum_{j=0}^{m}{}' D_{i\,j} T_i(X) T_j(Y) \qquad \text{.....(159)}$$

where $X = (2s - CA)/CB$

and $Y = (2p - DA)/DB$.

This may be rearranged to

$$h = \sum_{i=0}^{n}{}' T_i(X) \sum_{j=0}^{m}{}' D_{i\,j} T_j(Y) \quad .$$

Now the following may be written

$$B_i = \sum_{j=0}^{m}{}' D_{i\,j} T_j(Y)$$

where B_i is a function of pressure.

Hence

$$h = \sum_{i=0}^{n}{}' B_i T_i(X) \qquad \text{.....(160)}$$

and is also evaluated using relations (72) and (73). If equation (159) is to be evaluated along an isobar for various values of entropy or if iteration is to take place for entropy then all the B_i would be evaluated and equation (160), which is only a single power series, would be used instead of the double power series. Unfortunately for a once only evaluation of the equation this method is of no advantage. However this technique may be used in any of the Chebyshev equations and is especially valuable when iteration is being carried out.

This method is in contrast to equations composed of a conglomeration of terms which have been produced by a method of trial and error and hence have neither symmetry nor regularity of form. For this reason they usually have to be entirely re-evaluated through every iteration.

6.5.2 Combination of given variables

The Chebyshev equations can be written in the following form such that their properties can be more easily expressed,

$$h = h(p,s) \quad \text{(a)}$$

$$T = T(p,s) \quad \text{(b)}$$

$$v = v(p,s) \quad \text{(c)}.$$

The evaluation of the other properties for any given two can be divided into three categories as follows;

(1) Given p and s. Direct evaluations of (a), (b) and (c) give the properties h, T and v directly.

(2) Given p and h (or p and T or p and v). Direct interpolation in (a), (b) or (c) will enable s to be calculated and once this has been done the other two equations may then be evaluated directly. (The calculation is identical if s is given instead of p).

(3) Given h and T (or h and v or v and T). This is a rather complicated combination of properties as it requires iterpolation in both (a) and (b) to find p and s concurrently. For this case, as well as (2), a very simple equation which could be used to obtain a close approximation to the given data would be ideal, as interpolation in both equations would be a lengthy process.

Hence in order to reduce iteration in the calculation of thermodynamic properties it would be a definite advantage if some very simple equations in different variables were available in order to provide a very accurate initial guess. This technique, although it might look very clumsy at first sight, could well result in large savings of computer time.

6.6 Examination of accuracy of formulations

The only method for examining the accuracy of equations has been the comparison with the IST Tables values and tolerances. The only other method whichhas been suggested is the comparison with experimental data. This would

involve the introduction of a definite tolerance on the data which in some cases might prove rather difficult.

In order to avoid the above problem a suggestion, which may provide a more analytical method than either of the above, was made by Angus (101). This was the use of the 'characteristic curves', or curves on which the compressibility factor ($Z = pv/RT$) or its derivatives become zero, originally proposed by Brown (102) and discussed by him in great detail from a theoretical viewpoint. Further comments on the subject are contributed by Rowlinson (103) but, as far as is known, no examination of these curves has been made for a real fluid. It was decided to plot these curves for water using values obtained from Juza's formulation as it is the only equation which covers the necessary range - up to 100000 bar and 1000 ^{o}C. The curves as redefined by Angus may be represented by the conditions drawn up in Table 48. The first order curves J, A, B and C are the most useful and can be calculated fairly easily using numerical differentiation techniques. The second order curves are very much more complicated such that although many more are given by Brown, only the B_p and C_T curves are included.

According to Brown, the C curve intersects the J curve at its (the J curve) maximum and the B_p (or C_T) curve intersects the B curve at its maximum. On examining fig 26, which is a plot of the characteristic curves, this is seen to be the case. Unfortunately due to the limitation of the equation the curves cannot be continued outwith the temperature range 0 ^{o}C to 1000 ^{o}C and so the other conditions obtained by Brown cannot be checked. It would certainly appear, as suggested by Angus, that these requirements would provide very severe tests of formulations but unfortunately they occur outside the areas of general use of equations and for that reason they are unlikely to be of any use.

APPENDIX 1

Vapour pressure equations.

All the equations which are described in this Appendix have been used in Chapter 5. They are the most important and the most accurate of the equations which have been devised over the past thirty years. These equations are described along with their derivatives $\frac{dp}{dT}$ and their coefficients. In every case the equations have been modified to accept pressure in bars and temperature in degrees centigrade.

(1) Osborne, Stimson and Ginnings (1939)

These authors used two equations in calculating the saturation properties for their final paper. The first devised by Gerry for the temperature range $0^{o}C \leq t \leq 100^{o}C$ was rewritten by Bain in computing the NEL Tables to reduce the number of coefficients. However he had small round-off errors in two of the coefficients and these are corrected in the equation:

$$\log p = A + B \log z + Cz + \frac{D}{z}$$

where $z = t + 273.16$

$A = 28.590467$ $\quad B = -8.2$

$C = 2.4804_{10}{}^{-3}$ $\quad D = 3142.305.$

The derivative takes the form:

$$\frac{dp}{dT} = Np \left(\frac{B}{z} \cdot N + C - \frac{D2}{z}\right)$$

where $N = \ln 10 = 2.302595.$

For temperatures above $100^{o}C$ the correlation of Osborne and Meyers was used.

$$\log p = a + \frac{b}{z} + \frac{cx}{z}(10^{dx^2} - 1) + e\, 10^{fy^{1.25}}$$

where $x = z^2 - g$

$y = 374.11 - t$

$a = 5.432\ 368$ $\quad b = -2.0051_{10}{}^{3}$

$c = 1.3869_{10}{}^{-4}$ $\quad d = 1.1965_{10}{}^{-11}$

$e = -4.4_{10}{}^{-3}$ $\quad f = -5.7148_{10}{}^{-3}$

$g = 2.937_{10}{}^{5}.$

The derivative is expressed thus:

$$\frac{dp}{dT} = Np\left[- \frac{b + cx(10^{dx^2} - 1)}{z^2} + 2c(10^{dx^2}(1 + 2Ndx^2) - \frac{5}{4} NEF\ y^{0.25}\ 10^{Fy^{1.25}}\right]$$

---

(2) Steltz and Silvestri (1958)

Two equations are required in this formulation. The first covers the range 10 ^{o}C $\leq$ t $\leq$ 93.3 ^{o}C.

$$\log \frac{p_{crit}}{p} = \frac{x}{T} \cdot \frac{y}{z}$$

where $y = A + Bx + Cx^3$

$z = 1 + Dx$

$T = t + 273.15$

$x = T_{crit} - T$

$T_{crit} = 647.27\ ^{o}K$ $\qquad$ $p_{crit} = 221.058$ bar

$A = 3.2437814$ $\qquad$ $B = 5.86826_{10}{}^{-3}$

$C = 1.1702379_{10}{}^{-8}$ $\qquad$ $D = 2.1878462_{10}{}^{-3}$

$$\frac{dp}{dT} = -Np\ \{\frac{x\ Dy - (B + 3Cx^2)z}{Tz^2} - \frac{T_{crit} \cdot y}{T^2 \cdot z}\}$$

The second equation covers the range 93.3 ^{o}C $\leq$ t $\leq$ 373.89 ^{o}C

$$\log\frac{p_{crit}}{p} = \frac{x}{T}\frac{Y}{Z}$$

where $Y = a + bx + cx^3 + dx^4$

$Z = 1 + dx$

$a = 2.386313$ $\qquad$ $b = 4.14113_{10}{}^{-2}$

$c = 7.515484_{10}{}^{-9}$ $\qquad$ $d = 1.3794481_{10}{}^{-2}$

$e = 6.56444_{10}{}^{-11}$

$$\frac{dp}{dT} = - Np\{\frac{x[dY - (b + 3cx^2 + 4ex^3)Z]}{T\ Z^2} - \frac{T_{crit}\ Y}{T^2\ Z}\}$$

---

(3) Bridgeman and Aldrich (1963)

This equation covers the entire saturation line from 0 °C up to the critical temperature (374.15 °C). It has been rewritten slightly to reduce the number of coefficients and to improve its presentation.

$$\log p = A + Y_1 - B(1 + Ct)Y_2$$

where $Y_1 = \frac{D\,X}{t + E}$

$$Y_2 = J(X - a)\left[187^2 - (X - a)^2\right]$$

$$X = t - 187$$

$$a = Z^2(1.87^2 - Z^2)/(F + Gt)$$

$$Z = H + K \cosh^{-1}\left(\frac{L}{t+M}\right)$$

$A = 1.0699498$ $\quad$ $B = 1.0137921$

$C = 5.83531_{10}{-4}$ $\quad$ $D = 4.16385282$

$E = 2.37098157_{10}2$ $\quad$ $F = 3.0231574_{10}{-1}$

$G = 3.377565_{10}{-3}$ $\quad$ $H = 2.44182356$

$J = 3.9730778_{10}{-9}$ $\quad$ $K = -4.31182356$

$L = 6.542906_{10}2$ $\quad$ $M = 2.66778_{10}2$.

The derivative of this equation was not calculated owing to its complexity and to the fact that values of the derivatives are tabulated in a paper by Bridgeman and Aldrich (62).

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(4) 1966 IFC K function

This equation appears in the '1966 Industrial Formulation' although it was superseded by the Japanese equation in the 'Improved' version. It is:

$$\beta = \exp(X) - Y$$

where $X = k_0 - k_3\theta^{-1} - k_4\theta^{-1}r\{1 - \exp(k_6 r^2)\} - k_7 \exp\{-43(k_8 - \theta)^{5/4}\}$

$$Y = -K_1(\theta - k_1)(\theta - k_2)\exp(-12\theta^4)$$

$$r = \theta^2 - k_5$$

$k_0 = 7.109304476$ $\quad k_1 = 4.22_{10}{}^{-1}$

$k_2 = 5.77_{10}{}^{-1}$ $\quad k_3 = 7.132345857$

$k_4 = 2.066561026_{10}{}^{-1}$ $\quad k_5 = 7.009_{10}{}^{-1}$

$k_6 = 4.8374$ $\quad k_7 = 1.062076810_{10}{}^{-2}$

$k_8 = 1.002$ $\quad K_1 = 4.4_{10}{}^{-5}$

$$\frac{dp}{dT} = \frac{P_c}{T_c}\left[\frac{dX}{d\theta}\cdot \exp(X) - \frac{dY}{d\theta}\right]$$

where $\frac{dX}{d\theta} = k_3\theta^{-2} - k_4\left[(2 - \theta^{-2}r)\{1 - \exp(k_6r^2)\} + 4\,k_6 r \exp(k_6r^2)\right] - k_7\cdot\frac{215}{4}$

$$(k_8 - \theta)^{\frac{1}{4}}.\exp\{-43(k_8 - \theta)^{5/4}\}$$

$$\frac{dY}{d\theta} = K_1\exp(-12\theta^4)\left[2\theta - k_1 - k_2 - 48\theta^3(\theta - k_1)(\theta - k_2)\right]$$

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(5) 1967 IFC K function

The Japanese have provided a number of correlations over the last few years and this is the one which was presented to the IFC as part of the Japanese proposed industrial formulation. It was prepared at Keio University, Tokyo in November 1965 and afterwards incorporated in the 'Improved 1966 Industrial Formulation'. It is:

$$\ln \beta = \frac{1}{\theta}\cdot\frac{X}{Y}$$

where $X = \sum_{i=1}^{5} K_i(1 - \theta)^i$

$$Y = 1 + K_6(1 - \theta) + K_7(1 - \theta)^2$$

$K_1 = -\ 7.6912\ 34564$ $\quad K_2 = -\ 2.6080\ 23696_{10}1$

$K_3 = -\ 1.6817\ 06546_{10}2$ $\quad K_4 = \ \ 6.4232\ 85504_{10}1$

$K_5 = -\ 1.1896\ 46225_{10}2$ $\quad K_6 = \ \ 4.1671\ 1732$

$K_7 = \ \ 2.0975\ 0676_{10}1$

$$\frac{dp}{dT} = \frac{p}{T_c\theta Y}\left\{\frac{dX}{d\theta} - \frac{X}{Y}\frac{dY}{d\theta} - \frac{X}{\theta}\right\}$$

where $\frac{dX}{d\theta} = \sum_{i=1}^{5} i\,K_i(1 - \theta)^{(i-1)}$

$$\frac{dY}{d\theta} = -K_6 - 2K_7(1 - \theta)$$

---

(6) API 44

This correlation only covers the temperature range $0\ ^{o}C \leq t \leq 150\ ^{o}C$ with 9 Antoine equations and is based on the unpublished results of Stimson. The form of the equation is

$$\log p \times 750.062 = A - \frac{B}{C+t}$$

where $0 \leq t < 30$	A = 8.184254	B = 1791.3	C = 238.1
$30 \leq t < 40$	A = 8.1393986	B = 1767.262	C = 236.29
$40 \leq t < 50$	A = 8.0886767	B = 1739.351	C = 234.10
$50 \leq t < 60$	A = 8.0464202	B = 1715.429	C = 232.14
$60 \leq t < 70$	A = 8.0116295	B = 1695.167	C = 230.41
$70 \leq t < 80$	A = 7.9845588	B = 1678.948	C = 228.97
$80 \leq t < 90$	A = 7.9634288	B = 1665.924	C = 227.77
$90 \leq t < 100$	A = 7.9483960	B = 1656.390	C = 226.86
$100 \leq t \leq 150$	A = 7.9186968	B = 1636.909	C = 224.92

$$\frac{dp}{dT} = \frac{p \times B}{750.062(C + t)^2}$$

---

(7) Gibson and Bruges (1966)

The two equations given here with their derivatives are those fully described in 5.3.1 and 5.3.2 and their coefficients are given in Appendix II.

The first or primary equation which has been used in the 1968 IFC Formulation for Scientific and General Use (104) may be written

$$Y = \ln \beta = \sum_{r=0}^{11} a_r T_r(x)$$

where $$x = \{2(^{1}/\theta - .95)^{.4} - a_{12}\}/a_{13}$$

$$\frac{dp}{dT} = -\frac{0.8\ T_c}{a_{13}} \frac{p}{T^2} (^{1}/\theta - .95)^{-.6} \cdot \frac{dY}{dx}$$

where $\frac{dY}{dx}$ is the derivative expressed by

$$\frac{dY}{dx} = \sum_{x=0}^{10} A_x T_x(x)$$

the coefficients A_x being calculated by the formula in 3.8.3.

The secondary equation gives a similar form of derivative. The equation is expressed by

$$Z = \frac{1}{\theta} = \sum_{x=0}^{11}{}' b_x T_x(y)$$

$$\text{where } y = (2[\ln(\tfrac{1}{\beta})]^{.4} - b_{12})/b_{13}$$

and the derivative by

$$\frac{dz}{dx} = \frac{b_{13}}{.8\alpha} \cdot \frac{2}{y_2}[\ln(\tfrac{1}{\beta})]^{.6} \frac{dY}{dx} \quad .$$

APPENDIX II

Summary of saturation equations and coefficients

Specific entropy of saturated vapour

$$s_g = \sum_{r=0}^{9}{}' A_r T_r(m)$$

where $m = 1 - A_{10}[\ln(1/\beta)]^{0.3}$

Equation (132)

A_0	$1.1835\,076\times10^{1}$	A_6	$2.5364\,843\times10^{-3}$
A_1	$-2.1272\,558$	A_7	$-1.7939\,573\times10^{-3}$
A_2	$7.6163\,359\times10^{-1}$	A_8	$-2.8016\,014\times10^{-3}$
A_3	$-2.0397\,835\times10^{-1}$	A_9	$8.5911\,506\times10^{-4}$
A_4	$1.0137\,278\times10^{-1}$	A_{10}	$9.8788\,522\times10^{-1}$
A_5	$-4.2114\,799\times10^{-2}$		

Specific entropy of saturated liquid

$$s_f = \sum_{r=0}^{7}{}' B_r T_r(M)$$

where $M = 1 - B_8[\ln(1/\beta)]^{0.2}$

Equation (133)

B_0	$5.9011\,350$	B_5	$-2.0115\,922\times10^{-2}$
B_1	$2.0984\,300$	B_6	$1.1878\,173\times10^{-3}$
B_2	$-7.7074\,519\times10^{-1}$	B_7	$4.0439\,196\times10^{-3}$
B_3	$1.2073\,121\times10^{-1}$	B_8	$1.2497\,246$
B_4	$2.1924\,890\times10^{-2}$		

Vapour pressure of saturated water

(basic equation)

$$\ln\beta = \sum_{r=0}^{n}{}' a_r T_r(x)$$

where $x = \{2(\frac{1}{\theta} - 0.95)^{0.4} - a_{n+1}\}/a_{n+2}$

n = 11 in (137)

n = 12 in (137b)

Equation (137)

a_0	$-8.1193\,642$	a_7	$1.2455\,399\times10^{-4}$
a_1	$5.1322\,555$	a_8	$-4.9154\,288\times10^{-5}$
a_2	$-1.1842\,407$	a_9	$4.6302\,565\times10^{-5}$
a_3	$1.1779\,592\times10^{-1}$	a_{10}	$1.5301\,334\times10^{-5}$
a_4	$-5.1576\,420\times10^{-3}$	a_{11}	$-2.0954\,530\times10^{-5}$
a_5	$-1.4689\,537\times10^{-3}$	a_{12}	$1.4522\,0717$
a_6	$5.3622\,818\times10^{-4}$	a_{13}	$-0.8487\,8953$

Equation (137b)

a_0	$-8.1191\,822$	a_8	$-7.1680\,688\times10^{-5}$
a_1	$5.1321\,021$	a_9	$7.0116\,127\times10^{-5}$
a_2	$-1.1841\,669$	a_{10}	$-1.3369\,480\times10^{-5}$
a_3	$1.1780\,993\times10^{-1}$	a_{11}	$7.2621\,013\times10^{-6}$
a_4	$-5.2291\,339\times10^{-3}$	a_{12}	$-1.2413\,833\times10^{-5}$
a_5	$-1.3829\,260\times10^{-3}$	a_{13}	$1.4522\,0717$
a_6	$4.7091\,300\times10^{-4}$	a_{14}	$-0.8487\,8953$
a_7	$1.6236\,398\times10^{-4}$		

Vapour pressure of saturated water (supplementary equation)

$$\frac{1}{\theta} = \sum_{r=0}^{11}{}' b_r T_r(y)$$

where $y = \{2[\ln(\frac{1.1}{\beta})]^{0.4} - b_{12}\}/b_{13}$

Equation (138)

b_0	3.0452 937	b_7	$3.3650\,007\times10^{-5}$
b_1	$-6.8230\,952\times10^{-1}$	b_8	$-1.2342\,248\times10^{-5}$
b_2	$1.6411\,495\times10^{-1}$	b_9	$1.4826\,550\times10^{-6}$
b_3	$-2.0232\,165\times10^{-3}$	b_{10}	$-1.0211\,645\times10^{-6}$
b_4	$-1.9239\,111\times10^{-3}$	b_{11}	$-4.0908\,090\times10^{-6}$
b_5	$-5.7454\,942\times10^{-4}$	b_{12}	2.9609 4250
b_6	$6.8411\,554\times10^{-5}$	b_{13}	-2.1798 8801

Equation (138b)

b_0	3.0453 155	b_7	$3.8395\,850\times10^{-5}$
b_1	$-6.8232\,822\times10^{-1}$	b_8	$-1.4499\,785\times10^{-5}$
b_2	$1.6412\,395\times10^{-1}$	b_9	$4.3608\,220\times10^{-6}$
b_3	$-2.0218\,292\times10^{-3}$	b_{10}	$-3.0585\,463\times10^{-6}$
b_4	$-1.9323\,341\times10^{-3}$	b_{11}	$-6.0574\,987\times10^{-7}$
b_5	$-5.6427\,254\times10^{-4}$	b_{12}	2.9609 4250
b_6	$6.0579\,866\times10^{-5}$	b_{13}	-2.1798 8801

Specific volume of saturated liquid

$$\frac{1}{\chi} = \sum_{r=0}^{10}{}' c_r T_r(z)$$

where $z = 1 - 2(1 - \frac{t}{t_{cl}})^{0.4}$

Equation (139)

c_0	4.332 053	c_6	$-3.765\,370\times10^{-3}$
c_1	-1.107 796	c_7	$1.123\,345\times10^{-3}$
c_2	$-5.275\,102\times10^{-2}$	c_8	$-2.458\,266\times10^{-3}$
c_3	$2.173\,547\times10^{-2}$	c_9	$-1.425\,530\times10^{-3}$
c_4	$-1.754\,636\times10^{-2}$	c_{10}	$-1.304\,721\times10^{-3}$
c_5	$5.125\,009\times10^{-3}$		

Saturated liquid α equation

$$\frac{\alpha}{p_{cl}v_{cl}} = \sum_{r=0}^{11}{}' d_r T_r(Q)$$

where $Q = \{2(\frac{1}{\theta} - 0.99)^{0.5} - d_{12}\}/d_{13}$

Equation (140)

d_0	2.62 821	d_7	$8.949\,914\times10^{-5}$
d_1	1.164 542	d_8	$-2.309\,905\times10^{-5}$
d_2	$-1.529\,470\times10^{-2}$	d_9	$1.352\,658\times10^{-5}$
d_3	$-6.087\,624\times10^{-2}$	d_{10}	$-5.909\,329\times10^{-6}$
d_4	$-1.233\,320\times10^{-2}$	d_{11}	$-2.335\,760\times10^{-6}$
d_5	$6.246\,461\times10^{-4}$	d_{12}	1.2746 319
d_6	$6.365\,584\times10^{-4}$	d_{13}	-1.0746 319

Specific enthalpy of saturated vapour

$$\frac{1}{\epsilon} = \sum_{r=0}^{10}{}' e_r T_r(w)$$

where $w = 1 - e_{11}(\frac{1}{\theta} - 1)^{0.4}$

and $\frac{1}{\epsilon} = \frac{p_{cl}v_{cl}}{hg}$

Equation (143)

e_0	$5.600\,998\times10^{-1}$	e_6	$-1.394\,169\times10^{-4}$
e_1	$2.298\,094\times10^{-2}$	e_7	$-1.841\,311\times10^{-4}$
e_2	$2.908\,374\times10^{-2}$	e_8	$-1.087\,239\times10^{-4}$
e_3	$5.286\,767\times10^{-3}$	e_9	$-4.918\,106\times10^{-5}$
e_4	$-7.390\,192\times10^{-4}$	e_{10}	$-2.310\,695\times10^{-5}$
e_5	$-3.042\,949\times10^{-4}$	e_{11}	1.763 847

APPENDIX III

Algol Programmes

In this appendix the programme using Clenshaw's modification to Forsythe's method of curve fitting is printed along with its flow chart. This version does not include the facility for either weighting or constraining but these can be easily introduced using the description in Chapter 3, since only three or four lines need to be altered for each case. The surface fitting programmes are based on the curve fitting routine such that the main difference in all the programmes is to be found in the input and output facilities.

A. Programme for curve fitting by orthogonal Chebyshev polynomials.

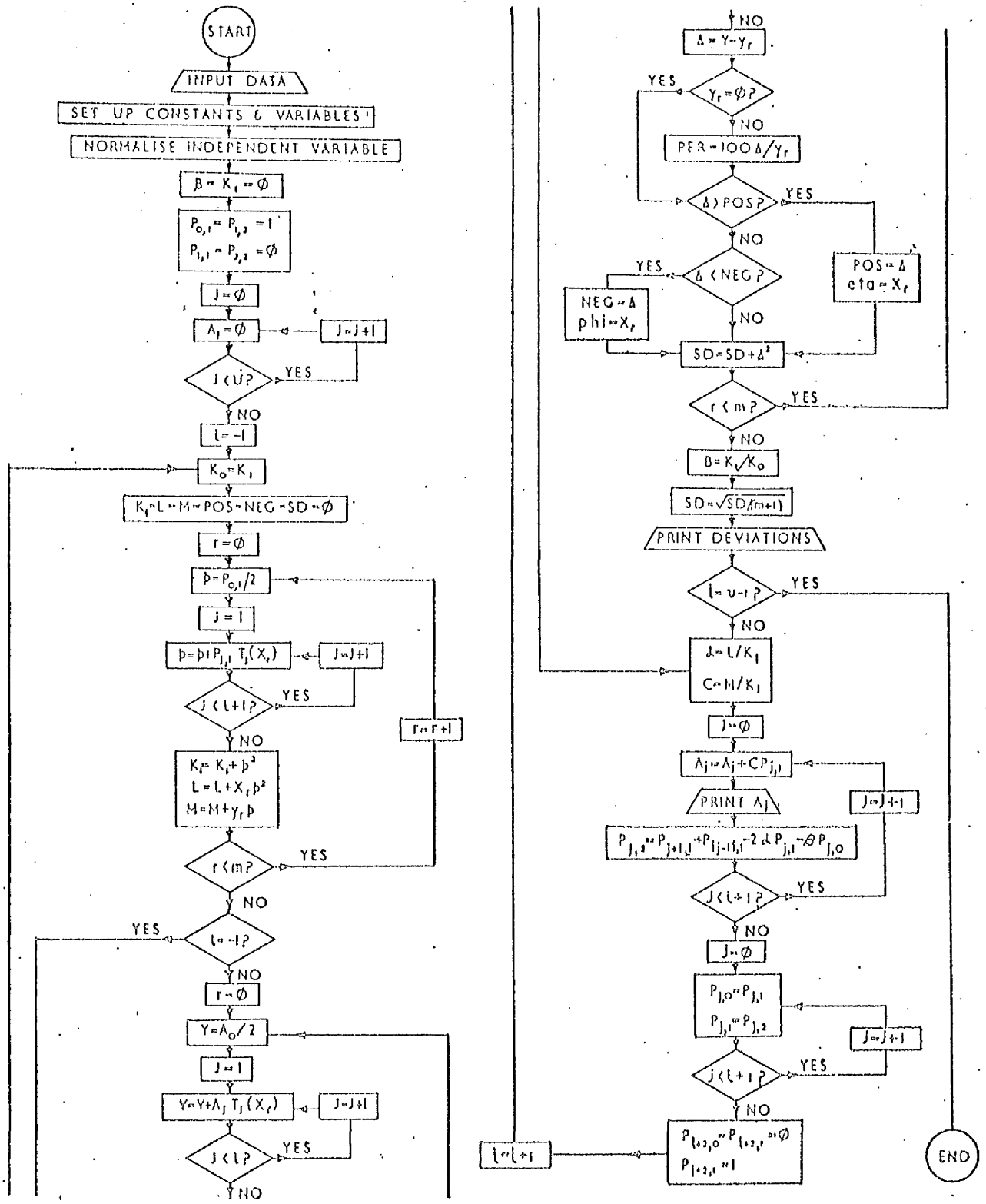
```
begin integer m,v,r,i,j,N,D,fa,fb,fc,fd,fe,l,mm,ii,ff,V;
    real xc,yc,xF,yF,k,C,a,b,L,M,KO,K1,POS,NEG,MAX,SD,eta,phi,mu,
    c,alpha,beta,p,delta,per,Y;
    boolean bool;
    real array x,y,xx,yy,del,YY[1:1000],T,A[0:25],P[0:25,0:2];
    fa:=format([sss-d.ddd10+nd]);
    fb:=format([sssss-d.dddd10+nd]);
    fc:=format([-d.ddddsddddsddd10-ndc]);
    fd:=format([-ndsss]);
    fe:=format([-ndddd.dddsss]);
    ff:=format([sss-d.dddddd10+nd]);
    open(20); open(70);
    mm:=read(20);
    for ii:=1 step 1 until mm do
    begin m:=read(20);
        if m<0 then
        begin m:=abs(m);
            for r:=1 step 1 until m do
            begin x[r]:=read(20);
                y[r]:=read(20);
            end;
        end
        else
        begin for r:=1 step 1 until m do
            x[r]:=read(20);
            for r:=1 step 1 until m do
            y[r]:=read(20);
        end;
```

```
N:=read(20);
for 1:=1 step 1 until N do
begin comment set up variables and constants;
    switch SW:=L1,L2;
    D:=read(20); v:=read(20); C:=read(20);
    k:=read(20); xc:=read(20); yc:=read(20);
    xF:=read(20); yF:=read(20);
    bool:=read boolean(20); V:=read(20);
    write text(70,[[p3c2s]D[9s]C[11s]K[10s]XC
    [10s]YC[10s]XF[10s]YF[c]]);
    write(70,fd,D);
    write(70,fe,C); write(70,fe,k);
    write(70,fe,xc); write(70,fe,yc);
    write(70,fe,xF); write(70,fe,yF);
    xc:=xc+xF; yc:=yc+yF;
    if x[1]>x[m] then write text(70,[[2c]VALUES*
    OF*X*SHOULD*BE*INCREASING*NOT*DECREASING.
    [2c]TO*OBTAIN*CORRECT*RESULTS*WHEN*EVALUATING
    *THE*POLYNOMIAL*EITHER*CHANGE*THE*SIGN*OF*
    B-A[2c]OR*CHANGE*THE*SIGNS*OF*THE*EVEN*
    COEFFICIENTS[4c]]);
    if D<0 then
    begin a:=read(20)+xF; b:=read(20)+xF;
        D:=abs(D);
    end
    else begin a:=x[1]+xF; b:=x[m]+xF; end;
    goto SW[D];
```

```
L1: a:=(a/xc-C)↑k; b:=(b/xc-C)↑k; a:=a+b; b:=2×b-a;
    for r:=1 step 1 until m do
    begin yy[r]:=(y[r]+yF)/yc;
        xx[r]:=(2×((x[r]+xF)/xc-C)↑k-a)/b;
    end;
    goto LL;
L2: a:=(a/xc-C)↑k; b:=(b/xc-C)↑k;
    a:=a+b; b:=2×b-a;
    for r:=1 step 1 until m do
    begin yy[r]:=ln((y[r]+yF)/yc);
        xx[r]:=(2×((x[r]+xF)/xc-C)↑k-a)/b;
    end;
LL: beta:=K1:=0.0; T[0]:=1.0;
    P[0,1]:=P[1,2]:=1.0; P[1,1]:=P[2,2]:=0.0;
    for j:=0 step 1 until v do
    A[j]:=0.0;
    for i:=-1 step 1 until v-1 do
    begin comment loop for calculating coefficients;
        K0:=K1;
        K1:=L:=M:=POS:=NEG:=MAX:=SD:=0.0;
        for r:=1 step 1 until m do
        begin p:=P[0,1]/2; T[1]:=xx[r];
            for j:=1 step 1 until i+1 do
            begin p:=p+P[j,1]×T[j];
                T[j+1]:=2×xx[r]×T[j]-T[j-1];
            end;
            K1:=K1+p↑2;
            L:=L+xx[r]×p↑2;
            M:=M+yy[r]×p;
        end;
        if i=-1 then goto first;
        for r:=1 step 1 until m do
```

```
begin comment calculation of deviations;
    Y:=A[0]/2; T[1]:=xx[r];
    for j:=1 step 1 until i do
    begin Y:=Y+A[j]×T[j];
        T[j+1]:=2×xx[r]×T[j]-T[j-1];
    end;
    delta:=if D=1 then yc×Y-yF-y[r]
    else if D=2 then yc×exp(Y)-yF-y[r]
    else 0.0;
    YY[r]:=delta+y[r];
    del[r]:=delta;
    if y[r]=0.0 then per:=0.0 else
    per:=100×delta/y[r];
    if delta>POS then
    begin POS:=delta;
        eta:=x[r];
    end
    else if delta<NEG then
    begin NEG:=delta;
        phi:=x[r];
    end;
    if abs(per)>abs(MAX) then
    begin MAX:=per;
        mu:=x[r];
    end;
    SD:=SD+delta↑2;
end;
beta:=K1/K0;
SD:=sqrt(SD/(m+1));
if bool and i>V then
begin write text(70,[[2c7s]X[14s]Y*OBS[11s]
   Y*EQN[12s]DEV[2c]]);
   for r:=1 step 1 until m do
```

```
                    begin write(70,ff,x[r]); write(70,ff,y[r]);
                        write(70,ff,YY[r]); write(70,fa,del[r]);
                        newline(70,1);
                    end;
                    newline(70,5);
                end;
                write text(70,[[c3s]MAX*POS*DEV[8s]X[9s]MAX*
                NEG*DEV[8s]X[8s]MAX*PER*DEV[9s]X[11s]S.D.[c]]);
                write(70,fa,POS); write(70,fb,eta);
                write(70,fa,NEG); write(70,fb,phi);
                write(70,fa,MAX); write(70,fb,mu);
                write(70,fa,SD);
                if i=v-1 then goto END;
        first:  alpha:=L/K1;
                c:=M/K1;
                write text(70,[[5c]COEFFICIENTS[c]]);
                for j:=0 step 1 until i+1 do
                begin A[j]:=A[j]+c×P[j,1];
                    write(70,fc,A[j]);
                    P[j,2]:=P[j+1,1]+P[abs(j-1),1]-2×alpha×
                            P[j,1]-beta×P[j,0];
                end;
                for j:=0 step 1 until i+1 do
                begin P[j,0]:=P[j,1];
                    P[j,1]:=P[j,2];
                end;
                P[i+2,0]:=P[i+3,1]:=0.0; P[i+2,1]:=1.0;
            end;
    END:end;
    end;
    close(20); close(70);
end→
```



Flow Chart for Curve Fitting Programme

APPENDIX IV

Tables of saturation properties

All the properties in this appendix have been calculated using the saturation equations (137), (139), (140) and (143) from Chapter 5 and the thermodynamic relations from Chapter 4. These relations are adequate for calculating the properties in the first three tables but for the calorimetric properties in the last two tables the partial derivatives $(\frac{\partial v}{\partial T})_p$ or $(\frac{\partial v}{\partial p})_T$ are required. In order to maintain thermodynamic consistency among the properties as far as possible only one of the derivatives was used. The other could then be calculated from the relation

$$(\frac{\partial v}{\partial T})_p = (\frac{dv}{dT})_\sigma - (\frac{\partial v}{\partial p})_T (\frac{dp}{dT})_\sigma \quad .$$

It was necessary to ensure that the most significant of the derivatives was used and this resulted in $(\frac{\partial v}{\partial p})_T$ being used for the liquid properties and $(\frac{\partial v}{\partial T})_p$ for the vapour properties. The derivatives were calculated from the 1968 IFC Formulation for Scientific and General Use and the values used were as follows:

t	$(\frac{\partial v}{\partial p})_f$	$(\frac{\partial v}{\partial T})_g$
°C	cm^3/g bar	cm^3/g K
0	$-5.0207_{10}-5$	$7.5699_{10}+2$
0.01	$-5.0204_{10}-5$	$7.5644_{10}+2$
10	$-4.7334_{10}-5$	$3.7719_{10}+2$
20	$-4.5627_{10}-5$	$1.9840_{10}+2$
30	$-4.4799_{10}-5$	$1.0955_{10}+2$
40	$-4.4642_{10}-5$	$6.3208_{10}+1$
50	$-4.5018_{10}-5$	$3.7950_{10}+1$
60	$-4.5831_{10}-5$	$2.3627_{10}+1$
70	$-4.7024_{10}-5$	$1.5206_{10}+1$
80	$-4.8564_{10}-5$	$1.0090_{10}+1$
90	$-5.0439_{10}-5$	$6.8864_{10}+0$
100	$-5.2652_{10}-5$	$4.8245_{10}+0$
110	$-5.5219_{10}-5$	$3.4631_{10}+0$
120	$-5.8170_{10}-5$	$2.5429_{10}+0$
130	$-6.1545_{10}-5$	$1.9072_{10}+0$
140	$-6.5401_{10}-5$	$1.4592_{10}+0$
150	$-6.9808_{10}-5$	$1.1376_{10}+0$
160	$-7.4860_{10}-5$	$9.0257_{10}-1$
170	$-8.0670_{10}-5$	$7.2810_{10}-1$
180	$-8.7385_{10}-5$	$5.9661_{10}-1$
190	$-9.5194_{10}-5$	$4.9616_{10}-1$
200	$-1.0434_{10}-4$	$4.1843_{10}-1$
210	$-1.1512_{10}-4$	$3.5762_{10}-1$
220	$-1.2797_{10}-4$	$3.0958_{10}-1$
230	$-1.4343_{10}-4$	$2.7132_{10}-1$
240	$-1.6224_{10}-4$	$2.4070_{10}-1$
250	$-1.8545_{10}-4$	$2.1614_{10}-1$
260	$-2.1450_{10}-4$	$1.9649_{10}-1$
270	$-2.5153_{10}-4$	$1.8092_{10}-1$
280	$-2.9969_{10}-4$	$1.6885_{10}-1$
290	$-3.6391_{10}-4$	$1.5989_{10}-1$
300	$-4.5221_{10}-4$	$1.5387_{10}-1$
310	$-5.7848_{10}-4$	$1.5081_{10}-1$
320	$-7.6876_{10}-4$	$1.5112_{10}-1$
330	$-1.0776_{10}-3$	$1.5578_{10}-1$
340	$-1.6398_{10}-3$	$1.6712_{10}-1$
350	$-3.0144_{10}-3$	$1.9173_{10}-1$
360	$-7.3736_{10}-3$	$2.7179_{10}-1$
370	$-6.2602_{10}-2$	$8.4735_{10}-1$
372	$-1.8462_{10}-1$	$1.5886_{10}+0$
374	$-6.0984_{10}+0$	$3.7862_{10}+1$
374.15	$-\infty$	∞

t	p	v_f	v_g	h_f	h_{fg}	h_g	s_f	s_{fg}	s_g
°C	bar	cm^3/g	cm^3/g	J/g	J/g	J/g	J/g K	J/g K	J/g K
0	0.006107	1.0002	206328	-0.03671	2500.8	2500.8	-0.0001	9.155	9.155
0.01	0.006112	1.0002	206185	0.006113	2500.8	2500.8	0.0000	9.155	9.155
10	0.012271	1.0004	106420	42.00	2477.1	2519.1	0.1510	8.749	8.900
20	0.023368	1.0018	57838	83.87	2453.7	2537.5	0.2963	8.370	8.666
30	0.042417	1.0044	32931	125.67	2430.1	2555.7	0.4365	8.016	8.453
40	0.073749	1.0078	19547	167.45	2406.3	2573.7	0.5721	7.684	8.256
50	0.123346	1.0121	12045	209.26	2382.2	2591.5	0.7035	7.372	8.075
60	0.19919	1.0171	7677.6	251.09	2357.9	2609.0	0.8310	7.078	7.909
70	0.31161	1.0227	5045.3	292.97	2333.2	2626.2	0.9548	6.799	7.754
80	0.47359	1.0290	3408.4	334.91	2308.2	2643.1	1.0752	6.536	7.611
90	0.70108	1.0360	2361.0	376.93	2282.8	2659.7	1.1925	6.286	7.478
100	1.01325	1.0435	1673.0	419.06	2256.7	2675.8	1.3069	6.048	7.355
110	1.4326	1.0516	1210.1	461.31	2230.1	2691.4	1.4185	5.820	7.239
120	1.9854	1.0603	891.74	503.7	2202.6	2706.3	1.528	5.602	7.130
130	2.7012	1.0697	668.36	546.3	2174.3	2720.6	1.634	5.393	7.026
140	3.6136	1.0798	508.69	589.1	2144.9	2734.0	1.739	5.192	6.931
150	4.7597	1.0905	392.60	632.1	2114.4	2746.6	1.842	4.997	6.838
160	6.1804	1.1020	306.86	675.5	2082.7	2758.1	1.942	4.808	6.751
170	7.9202	1.1143	242.62	719.1	2049.5	2768.6	2.042	4.625	6.667
180	10.027	1.1274	193.85	763.1	2014.9	2778.0	2.139	4.446	6.586
190	12.5522	1.1415	156.35	807.5	1978.5	2786.0	2.236	4.272	6.507
200	15.5505	1.1565	127.19	852.4	1940.4	2792.7	2.331	4.101	6.432
210	19.080	1.1727	104.264	897.7	1900.2	2797.9	2.425	3.933	6.358
220	23.201	1.1901	86.065	943.7	1857.8	2801.5	2.518	3.767	6.285
230	27.979	1.2088	71.478	990.3	1813.1	2803.3	2.610	3.603	6.214
240	33.480	1.2291	59.682	1037.6	1765.6	2803.2	2.702	3.441	6.143
250	39.776	1.2512	50.062	1085.8	1715.3	2801.0	2.793	3.279	6.072
260	46.940	1.2754	42.153	1134.9	1661.6	2796.5	2.885	3.117	6.001
270	55.051	1.3022	35.601	1185.2	1604.2	2789.4	2.976	2.954	5.930
280	64.191	1.3320	30.132	1236.8	1542.7	2779.4	3.068	2.789	5.857
290	74.448	1.3655	25.534	1289.9	1476.2	2766.1	3.161	2.621	5.782
300	85.917	1.4036	21.639	1344.8	1404.1	2748.9	3.255	2.450	5.705
310	98.697	1.4477	18.315	1402.1	1325.2	2727.2	3.351	2.272	5.623
320	112.90	1.4995	15.456	1462.2	1237.8	2700.0	3.449	2.087	5.536
330	128.65	1.5617	12.970	1525.9	1139.8	2665.7	3.552	1.890	5.441
340	146.08	1.6390	10.779	1594.8	1027.2	2621.9	3.660	1.675	5.336
350	165.37	1.741	8.804	1671.2	892.8	2564.0	3.779	1.433	5.212
360	186.74	1.893	6.943	1761.5	719.7	2481.2	3.916	1.137	5.053
370	210.53	2.225	4.936	1892.1	438.6	2330.8	4.113	0.682	4.795
372	215.62	2.382	4.406	1936.0	336.5	2272.5	4.180	0.522	4.701
374	220.84	2.800	3.503	2026.7	120.2	2146.9	4.318	0.186	4.504
374.15	221.23	3.15	3.15	2088	-0	2088	4.412	-0.000	4.412

t	p	$T\frac{dp}{dT}$	α	$\frac{d\alpha}{dT}$	β'	γ
^{o}C	bar	J/cm^3	J/g	J/g K	J/g	J/g
0	0.006107	0.0121207	-0.0006	4.2176	0.01212	2500.84
0.01	0.006112	0.0121290	0.0416	4.2175	0.01213	2500.81
10	0.012271	0.0232772	42.0257	4.1912	0.02329	2477.16
20	0.023368	0.0424236	83.8715	4.1796	0.04250	2453.70
30	0.042417	0.0737944	125.6405	4.1749	0.07412	2430.14
40	0.073749	0.1231068	167.3785	4.1730	0.12407	2406.39
50	0.123346	0.197787	209.1041	4.1722	0.20017	2382.41
60	0.19919	0.307155	250.8245	4.1719	0.31240	2358.20
70	0.31161	0.462552	292.5424	4.1717	0.47307	2333.72
80	0.47359	0.677413	334.2594	4.1717	0.69709	2308.92
90	0.70108	0.967283	375.9769	4.1718	1.00207	2283.76
100	1.01325	1.349776	417.6961	4.1720	1.40847	2258.14
110	1.4326	1.8445	459.42	4.1722	1.940	2232.00
120	1.9854	2.4729	501.14	4.1724	2.622	2205.23
130	2.7012	3.2584	542.86	4.1723	3.486	2177.75
140	3.6136	4.2255	584.58	4.1719	4.563	2149.48
150	4.7597	5.4007	626.30	4.1710	5.890	2120.31
160	6.1804	6.8115	668.00	4.1697	7.506	2090.18
170	7.9202	8.4863	709.69	4.1677	9.456	2058.99
180	10.0270	10.4549	751.36	4.1651	11.787	2026.65
190	12.5522	12.748	792.99	4.1619	14.55	1993.07
200	15.5505	15.396	834.59	4.1581	17.81	1958.16
210	19.080	18.432	876.15	4.1536	21.62	1921.80
220	23.201	21.889	917.66	4.1486	26.05	1883.87
230	27.979	25.802	959.12	4.1430	31.19	1844.24
240	33.480	30.206	1000.52	4.1369	37.13	1802.76
250	39.776	35.141	1041.86	4.1305	43.97	1759.23
260	46.940	40.648	1083.13	4.1237	51.84	1713.45
270	55.051	46.773	1124.33	4.1166	60.91	1665.16
280	64.191	53.565	1165.46	4.1092	71.35	1614.02
290	74.448	61.082	1206.51	4.1017	83.41	1559.64
300	85.917	69.389	1247.49	4.0940	97.40	1501.50
310	98.697	78.562	1288.39	4.0861	113.74	1438.89
320	112.90	88.694	1329.21	4.0780	133.00	1370.82
330	128.65	99.909	1369.95	4.0697	156.03	1295.80
340	146.08	112.38	1410.61	4.0613	184.20	1211.36
350	165.37	126.41	1451.18	4.0528	220.06	1112.89
360	186.74	142.52	1491.66	4.0444	269.85	989.56
370	210.53	161.83	1532.07	4.0362	360.13	798.76
372	215.62	166.25	1540.14	4.0340	395.94	732.44
374	220.84	170.91	1548.20	4.0306	478.53	598.73
374.15	221.23	171.27	1548.81	4.0302	539.18	539.07

t	u_f	u_g	g_f	g_g	f_f	f_g
^oC	J/g	J/g	J/g	J/g	J/g	J/g
0	-0.036681	2374.8	0.00	0.00	0.00	-126.01
0.01	0.005502	2374.8	0.00	0.00	0.00	-126.02
10	42.0	2388.6	-0.76	-0.76	-0.76	-131.35
20	83.9	2402.4	-3.00	-3.00	-3.00	-138.16
30	125.7	2416.1	-6.66	-6.66	-6.67	-146.35
40	167.4	2429.6	-11.71	-11.71	-11.72	-155.87
50	209.2	2442.9	-18.09	-18.09	-18.10	-166.66
60	251.1	2456.0	-25.75	-25.75	-25.77	-178.68
70	292.9	2469.0	-34.67	-34.67	-34.71	-191.89
80	334.9	2481.7	-44.81	-44.81	-44.86	-206.23
90	376.9	2494.2	-56.13	-56.13	-56.20	-221.65
100	419.0	2506.3	-68.59	-68.59	-68.70	-238.11
110	461.2	2518.0	-82.18	-82.18	-82.33	-255.54
120	503.5	2529.3	-96.85	-96.85	-97.06	-273.90
130	546.0	2540.0	-112.59	-112.59	-112.88	-293.12
140	588.7	2550.2	-129.36	-129.36	-129.75	-313.18
150	631.6	2559.7	-147.14	-147.14	-147.66	-334.00
160	674.8	2568.5	-165.90	-165.90	-166.59	-355.56
170	718.2	2576.5	-185.63	-185.63	-186.52	-377.80
180	762.0	2583.6	-206.30	-206.30	-207.43	-400.67
190	806.1	2589.8	-227.89	-227.89	-229.32	-424.14
200	850.6	2594.9	-250.38	-250.38	-252.18	-448.16
210	895.5	2599.0	-273.74	-273.74	-275.98	-472.68
220	940.9	2601.8	-297.97	-297.97	-300.73	-497.65
230	986.9	2603.3	-323.04	-323.04	-326.42	-523.02
240	1033.5	2603.4	-348.93	-348.93	-353.04	-548.74
250	1080.8	2601.9	-375.62	-375.62	-380.60	-574.75
260	1128.9	2598.7	-403.11	-403.11	-409.10	-600.98
270	1178.0	2593.5	-431.37	-431.37	-438.54	-627.36
280	1228.2	2586.0	-460.39	-460.39	-468.94	-653.81
290	1279.7	2576.0	-490.15	-490.15	-500.31	-680.24
300	1332.8	2563.0	-520.64	-520.64	-532.70	-706.55
310	1387.8	2546.5	-551.84	-551.84	-566.13	-732.61
320	1445.2	2525.5	-583.74	-583.74	-600.67	-758.24
330	1505.8	2498.9	-616.34	-616.34	-636.43	-783.19
340	1570.8	2464.5	-649.60	-649.60	-673.55	-807.06
350	1642.4	2418.4	-683.53	-683.53	-712.32	-829.12
360	1726.1	2351.5	-718.11	-718.11	-753.47	-847.77
370	1845.3	2226.9	-753.33	-753.33	-800.18	-857.24
372	1884.7	2177.5	-760.45	-760.45	-811.80	-855.44
374	1964.9	2069.5	-767.59	-767.59	-829.42	-844.96
374.15	2018	2018	-768.13	-768.13	-837.8	-837.8

Saturated liquid properties

t	α_σ	α_p	β_T	β_s	γ_σ	γ_v	c_σ	c_p	c_v	W
°C	K^{-1}	K^{-1}	cm^3/J	cm^3/J	J/cm^3K	J/cm^3K	J/g K	J/g K	J/g K	m/s
0	$-4.765_{10}-5$	$-4.762_{10}-5$	$5.020_{10}-4$	$5.018_{10}-4$	$4.437_{10}-5$	-0.0949	4.218	4.2183	4.2171	1411.8
0.01	$-4.750_{10}-5$	-4.748_{10} 5	$5.020_{10}-4$	$5.018_{10}-4$	$4.440_{10}-5$	-0.0946	4.218	4.2183	4.2171	1411.8
10	$8.665_{10}-5$	$8.669_{10}-5$	$4.732_{10}-4$	$4.726_{10}-4$	$8.221_{10}-5$	0.1832	4.193	4.1926	4.1881	1454.8
20	$2.009_{10}-4$	$2.010_{10}-4$	$4.554_{10}-4$	$4.526_{10}-4$	$1.447_{10}-4$	0.4413	4.182	4.1819	4.1559	1487.8
30	$2.989_{10}-4$	$2.990_{10}-4$	$4.460_{10}-4$	$4.395_{10}-4$	$2.434_{10}-4$	0.6703	4.179	4.1786	4.1176	1511.6
40	$3.838_{10}-4$	$3.840_{10}-4$	$4.430_{10}-4$	$4.318_{10}-4$	$3.931_{10}-4$	0.8668	4.179	4.1788	4.0738	1527.7
50	$4.584_{10}-4$	$4.587_{10}-4$	$4.448_{10}-4$	$4.284_{10}-4$	$6.121_{10}-4$	1.0313	4.181	4.1809	4.0262	1537.1
60	$5.252_{10}-4$	$5.256_{10}-4$	$4.506_{10}-4$	$4.283_{10}-4$	$9.220_{10}-4$	1.1664	4.184	4.1845	3.9768	1541.1
70	$5.861_{10}-4$	$5.867_{10}-4$	$4.598_{10}-4$	$4.310_{10}-4$	$1.348_{10}-3$	1.2761	4.189	4.1896	3.9268	1540.5
80	$6.429_{10}-4$	$6.438_{10}-4$	$4.719_{10}-4$	$4.360_{10}-4$	$1.918_{10}-3$	1.3641	4.196	4.1963	3.8772	1536.2
90	$6.969_{10}-4$	$6.982_{10}-4$	$4.869_{10}-4$	$4.433_{10}-4$	$2.664_{10}-3$	1.4341	4.204	4.2050	3.8282	1528.8
100	$7.495_{10}-4$	$7.514_{10}-4$	$5.046_{10}-4$	$4.524_{10}-4$	$3.617_{10}-3$	1.4891	4.215	4.2158	3.7801	1518.7
110	$8.016_{10}-4$	$8.042_{10}-4$	$5.251_{10}-4$	$4.635_{10}-4$	$4.814_{10}-3$	1.5315	4.227	4.2290	3.7327	1506.3
120	$8.540_{10}-4$	$8.575_{10}-4$	$5.486_{10}-4$	$4.764_{10}-4$	$6.290_{10}-3$	1.5630	4.242	4.2447	3.6860	1491.9
130	$9.073_{10}-4$	$9.120_{10}-4$	$5.753_{10}-4$	$4.912_{10}-4$	$8.082_{10}-3$	1.5852	4.260	4.2632	3.6398	1475.7
140	$9.621_{10}-4$	$9.683_{10}-4$	$6.057_{10}-4$	$5.081_{10}-4$	$1.023_{10}-2$	1.5987	4.280	4.2848	3.5942	1457.8
150	$1.019_{10}-3$	$1.027_{10}-3$	$6.401_{10}-4$	$5.272_{10}-4$	$1.276_{10}-2$	1.6044	4.304	4.3096	3.5492	1438.2
160	$1.078_{10}-3$	$1.089_{10}-3$	$6.793_{10}-4$	$5.489_{10}-4$	$1.573_{10}-2$	1.6026	4.330	4.3381	3.5053	1416.9
170	$1.140_{10}-3$	$1.154_{10}-3$	$7.240_{10}-4$	$5.736_{10}-4$	$1.915_{10}-2$	1.5936	4.360	4.3705	3.4626	1393.8
180	$1.205_{10}-3$	$1.223_{10}-3$	$7.751_{10}-4$	$6.017_{10}-4$	$2.307_{10}-2$	1.5777	4.393	4.4074	3.4217	1368.8
190	$1.274_{10}-3$	$1.297_{10}-3$	$8.339_{10}-4$	$6.341_{10}-4$	$2.752_{10}-2$	1.5553	4.430	4.4493	3.3828	1341.8
200	$1.348_{10}-3$	$1.377_{10}-3$	$9.022_{10}-4$	$6.713_{10}-4$	$3.254_{10}-2$	1.5267	4.473	4.4970	3.3463	1312.6
210	$1.428_{10}-3$	$1.465_{10}-3$	$9.817_{10}-4$	$7.144_{10}-4$	$3.815_{10}-2$	1.4927	4.520	4.5515	3.3122	1281.2
220	$1.515_{10}-3$	$1.563_{10}-3$	$1.075_{10}-3$	$7.646_{10}-4$	$4.439_{10}-2$	1.4535	4.573	4.6137	3.2804	1247.6
230	$1.612_{10}-3$	$1.673_{10}-3$	$1.187_{10}-3$	$8.232_{10}-4$	$5.128_{10}-2$	1.4100	4.633	4.6854	3.2506	1211.8
240	$1.721_{10}-3$	$1.799_{10}-3$	$1.320_{10}-3$	8.918_{10} 4	$5.886_{10}-2$	1.3630	4.702	4.7684	3.2218	1174.0
250	$1.846_{10}-3$	$1.946_{10}-3$	$1.482_{10}-3$	$9.727_{10}-4$	$6.717_{10}-2$	1.3129	4.780	4.8655	3.1933	1134.1
260	$1.991_{10}-3$	$2.120_{10}-3$	$1.682_{10}-3$	$1.068_{10}-3$	$7.624_{10}-2$	1.2603	4.870	4.9803	3.1639	1092.6
270	$2.162_{10}-3$	$2.328_{10}-3$	$1.932_{10}-3$	$1.182_{10}-3$	$8.611_{10}-2$	1.2054	4.976	5.1178	3.1327	1049.4
280	$2.366_{10}-3$	$2.584_{10}-3$	$2.250_{10}-3$	$1.319_{10}-3$	$9.684_{10}-2$	1.1483	5.101	5.2650	3.0993	1004.7
290	$2.612_{10}-3$	$2.901_{10}-3$	$2.665_{10}-3$	$1.487_{10}-3$	$1.085_{10}-1$	1.0884	5.250	5.4921	3.0643	958.3
300	$2.913_{10}-3$	$3.303_{10}-3$	$3.222_{10}-3$	$1.697_{10}-3$	$1.211_{10}-1$	1.0251	5.433	5.7542	3.0304	909.5
310	$3.287_{10}-3$	$3.825_{10}-3$	$3.996_{10}-3$	$1.969_{10}-3$	$1.347_{10}-1$	0.9573	5.660	6.0948	3.0033	857.5
320	$3.764_{10}-3$	$4.531_{10}-3$	$5.127_{10}-3$	$2.341_{10}-3$	$1.495_{10}-1$	0.8838	5.951	6.5540	2.9924	800.4
330	$4.401_{10}-3$	$5.544_{10}-3$	$6.900_{10}-3$	$2.883_{10}-3$	$1.656_{10}-1$	0.8035	6.342	7.2069	3.0110	736.0
340	$5.325_{10}-3$	$7.159_{10}-3$	$1.000_{10}-2$	$3.740_{10}-3$	$1.833_{10}-1$	0.7155	6.903	8.2216	3.0737	662.0
350	$6.898_{10}-3$	$1.041_{10}-2$	$1.732_{10}-2$	$5.686_{10}-3$	$2.028_{10}-1$	0.6012	7.820	10.111	3.3202	553.3
360	$1.051_{10}-2$	$1.927_{10}-2$	$3.894_{10}-2$	$9.172_{10}-3$	$2.251_{10}-1$	0.4950	9.759	14.961	3.5237	454.3
370	$2.739_{10}-2$	$9.818_{10}-2$	$2.813_{10}-1$	$2.341_{10}-2$	$2.516_{10}-1$	0.3490	18.13	53.493	4.4518	308.3
372	$4.314_{10}-2$	$2.429_{10}-1$	$7.752_{10}-1$	$3.259_{10}-2$	$2.577_{10}-1$	0.3133	25.90	122.08	5.1316	270.3
374	$2.547_{10}-1$	6.007_{10} 0	2.178_{10} 1	$3.333_{10}-2$	$2.641_{10}-1$	0.2758	131.9	3006.2	4.6009	289.8
374.15	∞	∞	∞	∞	$2.646_{10}-1$	0.2646	∞	∞	∞	0.0

t	α_σ	α_p	β_T	β_s	γ_σ	γ_v	c_σ	c_p	c_v	W
°C	K^{-1}	K^{-1}	cm^3/J	cm^3/J	J/cm^3K	J/cm^3K	J/g K	J/g K	J/g K	m/s
0	-0.00694	3.669_{10}-3	1.639_{10}+3	1.226_{10}+3	4.437_{10}-5	2.239_{10}-6	-7.335	1.8397	1.3768	410.2
0.01	-0.00694	3.669_{10}-3	1.637_{10}+3	1.225_{10}+3	4.440_{10}-5	2.240_{10}-6	-7.335	1.8398	1.3768	410.2
10	-0.00649	3.544_{10}-3	8.154_{10}+2	6.133_{10}+2	8.221_{10}-5	4.347_{10}-6	-6.906	1.8736	1.4093	416.6
20	-0.00856	3.430_{10}-3	4.284_{10}+2	3.221_{10}+2	1.447_{10}-4	8.008_{10}-6	-6.539	1.8779	1.4122	423.7
30	-0.00547	3.327_{10}-3	2.362_{10}+2	1.774_{10}+2	2.434_{10}-4	1.408_{10}-5	-6.206	1.8781	1.4104	430.9
40	-0.00522	3.234_{10}-3	1.360_{10}+2	1.020_{10}+2	3.931_{10}-4	2.378_{10}-5	-5.898	1.8836	1.4129	437.8
50	-0.00467	3.151_{10}-3	8.140_{10}+1	6.102_{10}+1	6.121_{10}-4	3.871_{10}-5	-5.610	1.8965	1.4218	444.3
60	-0.00446	3.077_{10}-3	5.048_{10}+1	3.784_{10}+1	9.220_{10}-4	6.097_{10}-5	-5.341	1.9163	1.4364	450.5
70	-0.00456	3.014_{10}-3	3.232_{10}+1	2.422_{10}+1	1.348_{10}-3	9.324_{10}-5	-5.092	1.9417	1.4552	456.4
80	-0.00393	2.960_{10}-3	2.132_{10}+1	1.597_{10}+1	1.916_{10}-3	1.389_{10}-4	-4.863	1.9719	1.4771	462.0
90	-0.00355	2.917_{10}-3	1.444_{10}+1	1.080_{10}+1	2.664_{10}-3	2.020_{10}-4	-4.655	2.0065	1.5014	467.5
100	-0.00339	2.884_{10}-3	1.003_{10}+1	7.489_{10}+0	3.617_{10}-3	2.876_{10}-4	-4.466	2.0458	1.5280	472.6
110	-0.00343	2.862_{10}-3	7.123_{10}+0	5.306_{10}+0	4.814_{10}-3	4.018_{10}-4	-4.297	2.0902	1.5571	477.5
120	-0.00365	2.852_{10}-3	5.168_{10}+0	3.836_{10}+0	6.290_{10}-3	5.518_{10}-4	-4.148	2.1408	1.5891	482.1
130	-0.00384	2.854_{10}-3	3.823_{10}+0	2.825_{10}+0	8.082_{10}-3	7.465_{10}-4	-4.016	2.1986	1.6247	486.4
140	-0.00358	2.869_{10}-3	2.879_{10}+0	2.116_{10}+0	1.023_{10}-2	9.963_{10}-4	-3.901	2.2649	1.6642	490.3
150	-0.00525	2.898_{10}-3	2.205_{10}+0	1.610_{10}+0	1.276_{10}-2	1.314_{10}-3	-3.803	2.3407	1.7083	493.9
160	-0.00404	2.941_{10}-3	1.716_{10}+0	1.242_{10}+0	1.573_{10}-2	1.714_{10}-3	-3.721	2.4272	1.7571	497.0
170	-0.00295	3.001_{10}-3	1.355_{10}+0	9.717_{10}-1	1.915_{10}-2	2.214_{10}-3	-3.654	2.5253	1.8108	499.7
180	-0.00196	3.078_{10}-3	1.085_{10}+0	7.694_{10}-1	2.307_{10}-2	2.836_{10}-3	-3.601	2.6361	1.8692	501.9
190	-0.00106	3.173_{10}-3	8.803_{10}-1	6.161_{10}-1	2.752_{10}-2	3.605_{10}-3	-3.564	2.7604	1.9321	503.7
200	-0.00024	3.290_{10}-3	7.232_{10}-1	4.986_{10}-1	3.254_{10}-2	4.549_{10}-3	-3.543	2.8996	1.9991	505.1
210	-0.00951	3.430_{10}-3	6.014_{10}-1	4.075_{10}-1	3.815_{10}-2	5.703_{10}-3	-3.536	3.0553	2.0699	505.9
220	-0.01886	3.597_{10}-3	5.060_{10}-1	3.360_{10}-1	4.439_{10}-2	7.108_{10}-3	-3.547	3.2294	2.1443	506.1
230	-0.01829	3.796_{10}-3	4.307_{10}-1	2.794_{10}-1	5.128_{10}-2	8.813_{10}-3	-3.575	3.4253	2.2222	505.8
240	-0.01779	4.033_{10}-3	3.708_{10}-1	2.342_{10}-1	5.886_{10}-2	1.088_{10}-2	-3.623	3.6474	2.3039	504.8
250	-0.01737	4.317_{10}-3	3.229_{10}-1	1.978_{10}-1	6.717_{10}-2	1.337_{10}-2	-3.694	3.9019	2.3900	503.1
260	-0.01703	4.661_{10}-3	2.845_{10}-1	1.682_{10}-1	7.624_{10}-2	1.638_{10}-2	-3.789	4.1977	2.4814	500.6
270	-0.01677	5.082_{10}-3	2.538_{10}-1	1.440_{10}-1	8.611_{10}-2	2.002_{10}-2	-3.915	4.5473	2.5794	497.3
280	-0.01660	5.604_{10}-3	2.293_{10}-1	1.240_{10}-1	9.684_{10}-2	2.444_{10}-2	-4.077	4.9676	2.6853	493.0
290	-0.01653	6.262_{10}-3	2.102_{10}-1	1.073_{10}-1	1.085_{10}-1	2.979_{10}-2	-4.284	5.4826	2.7999	487.7
300	-0.01659	7.111_{10}-3	1.957_{10}-1	9.340_{10}-2	1.211_{10}-1	3.633_{10}-2	-4.550	6.1268	2.9233	481.3
310	-0.01679	8.234_{10}-3	1.858_{10}-1	8.160_{10}-2	1.347_{10}-1	4.433_{10}-2	-4.896	6.9526	3.0542	473.8
320	-0.01720	9.777_{10}-3	1.804_{10}-1	7.152_{10}-2	1.495_{10}-1	5.419_{10}-2	-5.357	8.0462	3.1892	464.9
330	-0.01793	1.201_{10}-2	1.808_{10}-1	6.277_{10}-2	1.656_{10}-1	6.644_{10}-2	-5.999	9.5647	3.3217	454.5
340	-0.01920	1.550_{10}-2	1.893_{10}-1	5.500_{10}-2	1.833_{10}-1	8.190_{10}-2	-6.954	11.828	3.4359	442.7
350	-0.02154	2.178_{10}-2	2.135_{10}-1	4.770_{10}-2	2.028_{10}-1	1.020_{10}-1	-8.547	15.688	3.5046	429.6
360	-0.02675	3.914_{10}-2	2.927_{10}-1	4.202_{10}-2	2.251_{10}-1	1.337_{10}-1	-11.87	26.868	3.8569	406.5
370	-0.04845	1.717_{10}-1	8.746_{10}-1	3.839_{10}-2	2.516_{10}-1	1.962_{10}-1	-25.27	111.86	4.9080	358.6
372	-0.06865	3.606_{10}-1	1.666_{10}+0	3.561_{10}-2	2.577_{10}-1	2.165_{10}-1	-37.39	226.72	4.8464	351.8
374	-0.30132	1.081_{10}+1	4.206_{10}+1	4.406_{10}-2	2.641_{10}-1	2.569_{10}-1	-168.9	6302.1	6.6008	282.0
374.15	- ∞	∞	∞	∞	2.646_{10}-1	2.646_{10}-1	- ∞	∞	∞	0.0

APPENDIX V

Publications

1. 'New equations for the thermodynamic properties of saturated water in both the liquid and vapour phases', J. Mech. Eng. Sci., 9 (1), 24, 1967.

2. 'An equation of state for compressed water from 1 to 1000 bar and from 0 °C to 150 °C', J. Mech. Eng. Sci., October, 1968. [In press]

3. 'The dynamic viscosity of compressed water to 10 kilobar and steam to 1500 °C', J. Mech. Eng. Sci., October, 1968. [In press]

Submitted for publication

4. 'Calculation of the thermodynamic properties of water substance, allowance being made for the difference between the Thermodynamic and International Practical Temperature Scales'.

This proposed paper is not included in the Appendix since its content is almost identical to section 4 of Chapter 4.

NEW EQUATIONS FOR THE THERMODYNAMIC PROPEF OF SATURATED WATER IN BOTH THE LIQUID AND VAPOUR PHASES

By M. R. Gibson* and E. A. Bruges†

Equations in the form of Chebyshev polynomials are presented which enable the thermodynamic properties of saturated water in its liquid and vapour phases to be calculated in a systematic manner. In the equations defining the pressure–temperature relationship the authors have made allowance for certain unpublished observations of the National Bureau of Standards and these are considered in the section relating to vapour pressure. It is believed that the assembly of equations specify for the first time the saturated liquid and vapour boundaries whose properties have previously only been available in tabular form.

INTRODUCTION

THE PURPOSE of this paper is to unify the final results of Osborne, Stimson and Ginnings (1)‡ by providing equations suitable for use with electronic digital computers in place of the 'patchwork' of tables and correlations on which the final and definitive paper of these authors is based. The provision of these equations permits evaluation of all the state properties along the saturation line from the triple point of water to the critical point, thus providing the most important boundary, apart from the hypothetical gas curve, for any surface which purports to represent the thermodynamic properties of water in its liquid and vapour phases. In view of the rigour with which earlier work was reviewed by Osborne and his colleagues only work relating to the saturation line published since 1939 is considered here. The 1964 N.E.L. Steam Tables were accepted and used as input data along with certain calorimetric observations of the National Bureau of Standards.

In the paper reference is made to the 1966 Formulation (2) which was prepared by an international group working under the aegis of the Sixth International Conference on the Properties of Steam. This group has defined certain quantities which are listed in Appendix 2 and which the authors have adopted. This has involved the use of the symbol β for reduced pressure, necessitating the use of the quantity β' for the function $v_f T(\mathrm{d}p/\mathrm{d}T)$, originally termed β by Osborne. The unit of pressure is the b where reference to the Cragoe–Stimson correctio in which the unit of pressure is the normal at

The MS. of this paper was first received at the Institution on 25th May 1966 and in its revised form, as accepted by the Council for publication, on 16th September 1966. 33

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† *Reader, Mechanical Engineering Department, University of Glasgow. Associate Member of the Institution.*

‡ *References are given in Appendix 4.*

Notation

A, B, C	Constants.
a, b, c	Constants.
h	Specific enthalpy, J/g.
p, P	Pressure, bar, atm.
R	Gas constant, J/kg degK.
s	Specific entropy, J/g degK.
T	Temperature, °K.
T_t	Triple point of water temperature, 2
t	Temperature, °C, $T = t + 273{\cdot}15$.
u	Specific internal energy, J/g.
v	Specific volume, cm³/g.
α, β', γ	Properties of saturated liquid an defined by Osborne.
β	Reduced pressure. }
ϵ	Reduced enthalpy. }
θ	Reduced temperature. } Appendix 2
χ	Reduced volume. }

Subscripts

f, g	Refer to saturated liquid and va respectively.
t, c	Refer to the states at triple and crit respectively.

HISTORICAL BACKGROUND

During the period 1930 to 1939 a number of pa thermodynamic properties of saturated water i

liquid and vapour phases were published by Osborne and his associates of the National Bureau of Standards (3). These papers give not only the results obtained at the N.B.S. but include also a number of critical reviews of the work of earlier and contemporary experimenters. The final paper by Osborne, Stimson and Ginnings (1) summarizes in tabular form the results of all the investigations and this paper must be considered as definitive. In view of the importance of the N.B.S. researches a complete list is given under reference (3).

In deriving the equations presented here it was found necessary to refer to the smoothed calorimetric data from which Osborne, Stimson and Ginnings compiled their final paper. These observations were derived from experiments based on principles laid down by Osborne (4) prior to the commencement of the researches. Only three of these experiments need concern us here, although the relationship between pressure and temperature along the saturation line is also of fundamental importance.

(1) *Measurement of* α—constant mass experiment. This experiment leads to the determination of a quantity defined by Osborne as α, a symbol which it is convenient to retain along with the quantities β' and γ, defined below. The quantity, α, is a close approximation to the heat capacity of saturated liquid water, particularly at the lower temperatures. It may be shown that

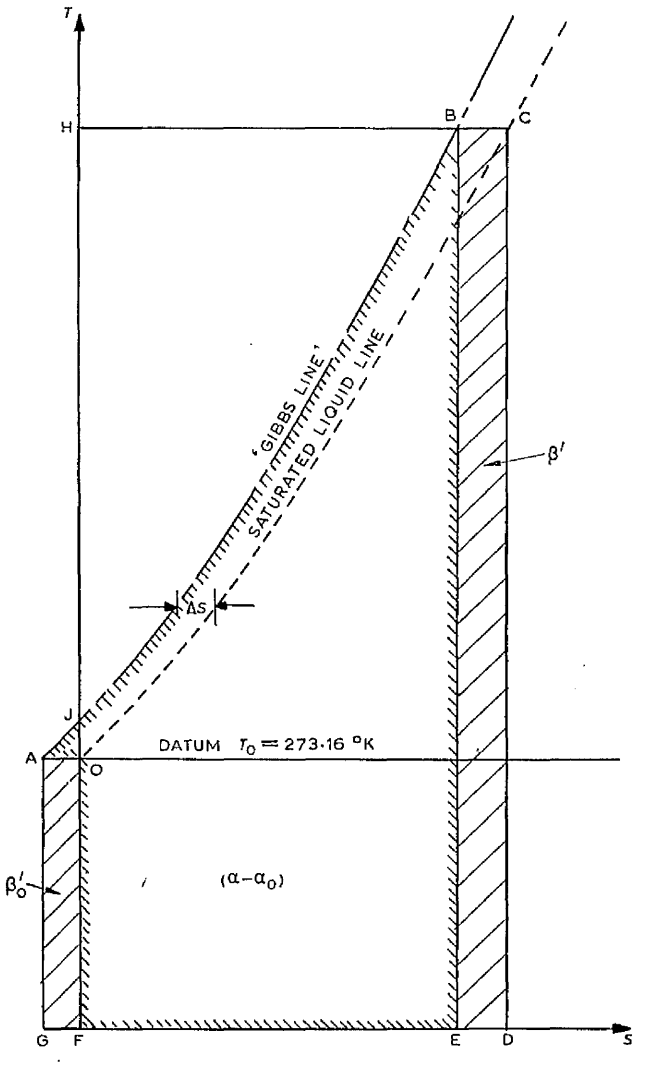
$$\alpha = h_f - Tv_f \frac{\mathrm{d}p}{\mathrm{d}T} \quad . \quad . \quad . \quad . \quad (1)$$

(2) *Measurement of* β'—an experiment in which saturated liquid is withdrawn from the calorimeter. It may be shown that

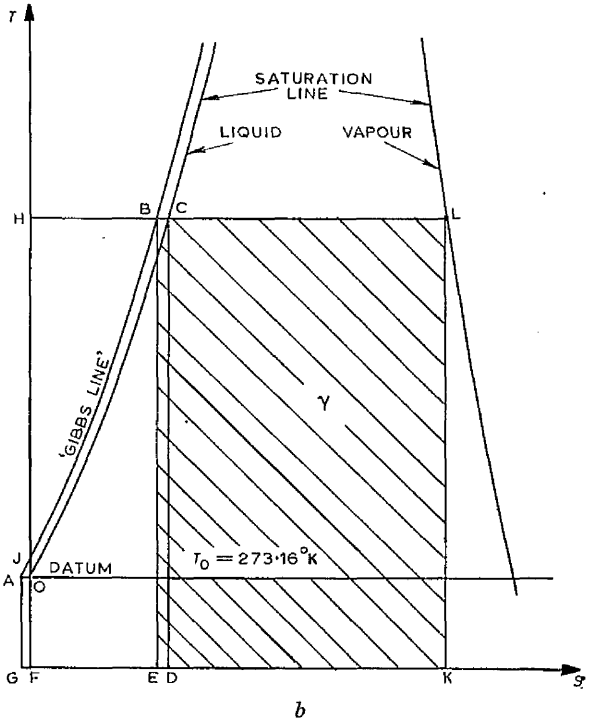
$$\beta' = v_f T \frac{\mathrm{d}p}{\mathrm{d}T} \quad . \quad . \quad . \quad . \quad (2)$$

(3) *Measurement of* γ—an experiment in which saturated vapour is withdrawn from the calorimeter. In this case a quantity, γ, is determined where

$$\gamma = v_g T \frac{\mathrm{d}p}{\mathrm{d}T} \quad . \quad . \quad . \quad . \quad (3)$$



a



b

The 'Gibbs line' lies to the left of the saturated liquid line by an amount Δs. $\Delta s = v_f(\mathrm{d}p/\mathrm{d}T)$ and at the datum temperature $\Delta s = 0{\cdot}000\ 044$ J/g degK. Thus the points O and A are almost coincidental.

Area OFGAO $= \beta'_0$.
Area CDEBC $= \beta' = v_f T(\mathrm{d}p/\mathrm{d}T)$.
Area OABEFO $= (\alpha - \alpha_0)$.
Area BLKEB $= \gamma = v_g T(\mathrm{d}p/\mathrm{d}T)$.
Area HBJH—area OAJO $= -[g_f] = -[h_f - T_0 S_f]$.

Fig. 1. *Representation of the quantities* α, β' *and* γ *on the T–S diagram*

It is to be noted that the quantities α, β' and γ are functions of temperature and that, if the saturation pressure, p, and the specific volume of the saturated liquid, v_f, are also expressed as functions of temperature it is relatively easy to generate a complete table of properties for the liquid and vapour phases using the equations given in Appendix 1. Further, Haywood (5) has shown that the quantities α, β' and γ may be represented as areas on a T–S diagram as indicated in Fig. 1.

In reformulating the N.B.S. measurements, which were given in international joules per gramme, it has been necessary to introduce a conversion factor relating the international joule (N.B.S.) value to the absolute joule or joule, there now being no difference between 'international' and 'absolute' units. Stimson (6) gave the conversion factor as

$$1 \text{ int J (N.B.S. value)} \equiv 1{\cdot}000\ 165 \text{ J}$$

In addition to taking account of the above conversion the authors have allowed for a change of datum state from 0°C to 0·01°C, which is the triple point of water temperature and is equivalent to 273·16°K exactly. At the triple point of water, which is now the datum for all steam tables, the internal energy and entropy are taken to be zero, whereas previously the enthalpy and entropy were each taken to be zero at 0°C.

The authors have treated the International Practical Scale and the Thermodynamic Celsius Scale of Temperature as being identical although some workers (7) (8) have shown the very small discrepancies that can arise if allowance is made for the small difference between the scales.

VAPOUR PRESSURE OF SATURATED WATER

When the work described in this paper was initiated the authors believed that the entries in the 1963 International Skeleton Tables (I.S.T.) represented the best possible interpretation of the vapour pressure measurements. While the work was in progress Dr Angus* drew the authors' attention to the existence of unpublished measurements which had been used by the American Petroleum Institute to specify the vapour pressure–temperature relationship at temperatures between 0°C and 100°C. These A.P.I. values differ by no more than 75×10^{-6} atm from the 1963 Skeleton Table values and are not outside the bounds of the Skeleton Table tolerances. In view of this confliction the authors decided to put forward two sets of equations, a first which is based directly on the 1963 Skeleton Tables and a second which takes account of the unpublished N.B.S. observations.

Vapour pressure equations based on 1963 Skeleton Tables

In the temperature range 0°C to 100°C the vapour pressures of saturated water in the 1963 I.S.T. are based on a correlation of Dr H. T. Gerry of the N.B.S. (1) which was itself based on the revised observations of Holborn and Henning (9). The original observations were fou unreliable due to an error in the temperature sc by the Physikalisch Technische Reichsanstalt. T was subsequently corrected by Henning and the c values were published in the Wärmetabellen (1c 100°C to the critical temperature (374·15°C) th pressure values in the 1963 I.S.T. are based on correlation of Osborne and Meyers (11).

A new equation relating the vapour pressure a perature of saturated water has been develope produce the entries in Table 1 of the 1964 N.E.I Tables (12). These 377 entries, which were used data, are themselves derived from the two equati of Gerry and that of Osborne and Meyers, g Osborne, Stimson and Ginnings (1) and are agreement with the values appearing in the 1 national Skeleton Tables. The equation is in the f Chebyshev series

$$\ln \beta = \sum_{r=0}^{11}{}' a_r T_r(x) \quad . \quad . \quad .$$

where $$x = \left\{2\left(\frac{1}{\theta} - 0{\cdot}95\right)^{0{\cdot}4} - A\right\} \Big/ B$$

A supplementary equation has also been d using the same notation and this has the form

$$\frac{1}{\theta} = \sum_{r=0}^{11}{}' b_r T_r(y) \quad . \quad . \quad . \quad .$$

where $$y = \left\{2\left[\ln\left(\frac{1{\cdot}1}{\beta}\right)\right]^{0{\cdot}4} - C\right\} \Big/ D$$

The equations have been expressed in dime form using values adopted by the Sixth Inte Conference on the Properties of Steam, New Yo as the nearest estimates at that time of the true the critical point. These quantities are given in Ap

Very little difficulty was experienced in fitting and an accuracy of one part in 15 000 (0·007 per better was obtained from an earlier form of the However, this earlier fit was unsatisfactory since vatives in the critical region were poor and, in the critical point dp/dT was zero due to the for equation then being used. It should be emphas in addition to achieving a high degree of acc reproducing the values of p, the derivatives dp/dT equations (4a) and (5a) should be smooth and ag closely with the values obtained by other worker the constants of the equation were changed sl give satisfactory derivatives (Table 2), coefficie obtained which gave p to an accuracy of one par (0·015 per cent) or better and these coefficients in Appendix 1. The quantity fitted was $\ln \beta$ and n ing was employed except in the vicinity of 100°C (where the equation must reproduce a value of N/m^2 exactly.

Table 1 compares the results from equation the values and tolerances on p, given in the 1963 tional Skeleton Tables, and with the values f saturation function K of the 1966 Formulation (2

* *Dr S. Angus, Scientific Director, I.U.P.A.C. Thermodynamic Tables Project Centre, Imperial College, London.*

be seen that, at the critical point, the difference between the value given by the proposed equation and the I.S.T. value is three-tenths of the tolerance, at 374°C it is six-tenths of the tolerance, while, apart from these points, the differences everywhere are about one-tenth of the tolerance or lower. At the temperature of 100°C the agreement is exact. The function K, on the other hand, gives larger differences in the critical region, varying from two-tenths to ten-tenths of the tolerance.

Table 1

Temperature, °C	Pressure, bar			
	Value and tolerance from International Skeleton Tables 1963	±	Value from equation (4a)	Value from saturation function K
*[0	0·006 108	0·000 006	0·006 107	0·006 108]
0·01	0·006 112	0·000 006	0·006 112	0·006 112
10	0·012 271	0·000 010	0·012 271	0·012 276
20	0·023 368	0·000 020	0·023 368	0·023 371
30	0·042 418	0·000 030	0·042 417	0·042 415
40	0·073 750	0·000 038	0·073 749	0·073 743
50	0·123 35	0·000 06	0·123 35	0·123 34
60	0·199 19	0·000 10	0·199 19	0·199 19
70	0·311 61	0·000 16	0·311 61	0·311 62
80	0·473 58	0·000 24	0·473 59	0·473 61
90	0·701 09	0·000 36	0·701 08	0·701 10
100	1·013 25	†	1·013 25	1·013 25
110	1·432 7	0·001 0	1·432 6	1·432 6
120	1·985 4	0·001 3	1·985 4	1·985 3
130	2·701 1	0·001 6	2·701 2	2·701 1
140	3·613 6	0·002 1	3·613 6	3·613 5
150	4·759 7	0·003 2	4·759 7	4·759 6
160	6·180 4	0·004 2	6·180 4	6·180 4
170	7·920 2	0·053	7·920 2	7·920 2
180	10·027	0·007	10·027	10·027
190	12·553	0·008	12·552	12·550
200	15·550	0·008	15·550	15·550
210	19·080	0·008	19·080	19·080
220	23·202	0·009	23·201	23·201
230	27·979	0·010	27·979	27·979
240	33·480	0·012	33·480	33·480
250	39·776	0·013	39·776	39·776
260	46·941	0·015	46·940	46·940
270	55·052	0·017	55·051	55·051
280	64·191	0·020	64·191	64·192
290	74·449	0·022	74·448	74·449
300	85·917	0·024	85·917	85·917
310	98·694	0·030	98·696	98·698
320	112·89	0·03	112·90	112·90
330	128·65	0·04	128·65	128·65
340	146·08	0·04	146·08	146·08
350	165·37	0·04	165·37	165·37
360	186·74	0·05	186·74	186·73
370	210·53	0·05	210·53	210·50
371	213·06	0·10	213·06	213·02
372	215·63	0·11	215·62	215·58
373	218·2	0·1	218·21	218·18
374	220·9	0·1	220·84	220·80
374·15 ±0·10	221·2	0·1	221·23	221·20

* The states here shown are not stable.
† The pressure at the saturated state has a tolerance which is zero when the temperature is 100°C on the International Practical Scale and is ±0·000 04 bar when the temperature is 100°C on the Thermodynamic Celsius Scale.

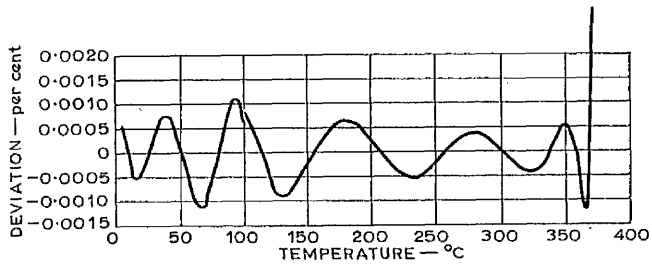


Fig. 2. *Percentage deviation of values given by equation (4a) from 1963 I.S.T. values*

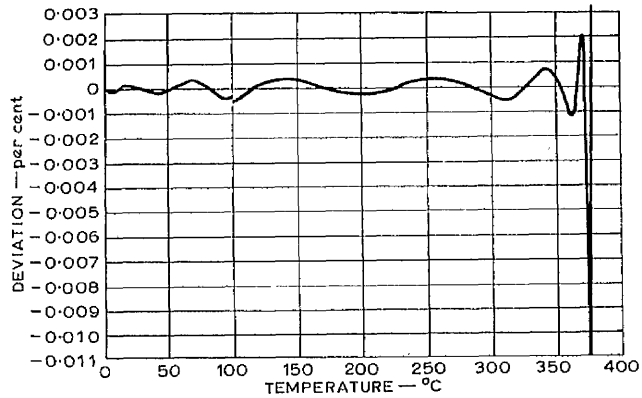


Fig. 3. *Percentage deviation of values given by equation (5a) from 1963 I.S.T. values*

Fig. 2 shows a plot of the percentage deviation against temperature for equation (4a) where the percentage deviation $= \left\{\frac{p_{eqn} - p_{IST}}{p_{eqn}}\right\} \times 100$ per cent.

As can be seen in Fig. 3, which is a similar plot for equation (5a), there is a small discontinuity at 100°C. This would appear to indicate that the two equations used by Osborne, Stimson and Ginnings do not merge perfectly in the vicinity of 100°C, a fact which is substantiated in the next section.

Table 2 compares the derivatives $\left(T\frac{dp}{dT}\right)$, of equation (4a) above 370°C with those of the N.B.S. (1932) (**13**), Egerton and Callendar (**14**), Keyes (M.I.T.) (**15**), N.B.S. (1939) (**1**), Bridgeman and Aldrich (**8**), and I.F.C. K function. At temperatures below 370°C the various correlations give derivatives which differ only slightly from one another, although above 300°C the I.F.C. K function gives values which are up to 1·5 per cent higher than those given by the other correlations. Above 370°C the effect of any differences among the correlations is most marked. The K values are undoubtedly on the high side and Keyes's values are low, there being reasonably good agreement among the remaining values. It is interesting to note that the average value, excluding that derived from

Table 2

t, °C	$T\frac{dp}{dT}$ (J/cm³)								
	N.B.S. 1932	Egerton and Callendar	Keyes (M.I.T.)	N.B.S. 1939	Bridgeman and Aldrich	K	Equation (4a)	Averages	
								With K	Without K
370	161·91	162·40	161·48	161·94	161·97	164·22	161·83	162·24	161·91
372	166·31	166·82	165·69	166·60	166·57	168·63	166·25	166·64	166·31
374	170·93	171·41	170·08	172·53	171·57	173·27	170·91	171·54	171·25
374·15	—	—	—	173·13	171·91	173·63	171·27	172·48	172·10

Table 3

a Equation (4a).

Temperature, °C	Pressure, bar	Temperature, °C
0·000	0·006 107	0·000
50·000	0·123 35	50·000
100·000	1·013 25	100·000
150·000	4·759 7	150·000
200·000	15·550	200·000
250·000	39·776	250·000
300·000	85·917	300·000
350·000	165·37	349·999
374·150	221·23	374·152

b Equation (5a).

Pressure, bar	Temperature, °C	Pressure, bar
0·006 107	−0·00	0·006 107
0·123 35	50·00	0·123 35
1·013 25	100·00	1·013 26
4·759 7	150·00	4·759 7
15·550	200·00	15·550
39·776	250·00	39·776
85·917	300·00	85·917
165·37	350·00	165·37
221·2	374·14	221·21

the K function, is close to the predicted values given by equation (4a) and by Bridgeman and Aldrich. The value of $\left(T\frac{dp}{dT}\right)_{crit}$ would appear to be close to 172 J/cm³.

Tables 3*a* and *b* illustrate the accuracy of equations (4a) and (5a) used in conjunction. For Table 3*a* one value of $T = T_1$ is fed into equation (4a) to give $p = p_1$, which is in turn put into equation (5a) to give $T = T_2$. As shown, the values T_1 and T_2 agree up to 350°C, after which there is a maximum error of one part in 18 000 (0·006 per cent). Table 3*b* was obtained by starting with the value of p and using the two equations in reverse order. The values of p were in complete agreement except at $t = 100$°C, where a maximum error of one part in 100 000 (0·001 per cent) was obtained.

Equation (5a) has been put forward as a supplementary equation since it was thought easier and quicker to use a second equation than to interpolate in the first. The constants for this second equation which gives an accuracy of one part in 11 000 (0·009 per cent), are given in Appendix 1.

Vapour pressure equations based on 'A.P.I. 44' between 0°C and 100°C

The relation between the pressure and temperature of water at saturation at low pressures is widely used as a reference by chemists investigating the vapour pressure of organic substances. It has recently come to light that the values for the vapour pressure of saturated water used by them are commonly not those given in the International Skeleton Tables, but those in Table 2-1-(1.01)-K of the American Petroleum Institute Research Project 44 (**16**), which differ from the 1963 I.S.T., and that some recent measurements are in conflict with both sources.

The A.P.I. 44 table uses as a basis the saturation table values of the 1934 I.S.T., generated from the 1934 correlation of Osborne and Meyers which was at that time considered valid from 0°C to 374·15°C, and added corrections derived from measurements made at the National Bureau of Standards in connection with a gas thermometry programme, by Stimson and Cragoe in 1942 and by Stimson and Wilson in 1948. These 'Cragoe–Stimson' corrections, as they are known, have never been published nor has the work upon which they are based, but they have received limited private circulation (**17**).

Table of 'Cragoe–Stimson' correlations

Corrections to be added to pressures given in Table 2 of Osborne and Meyers (**11**).

Temperature, °C	ΔP to be added, atm × 10⁻⁶
0	0
25	39
50	74
60	75
80	47
100	0

More recently Douslin (**18**), using an inclined piston gauge, has made observations on the vapour pressure of water in the range 0°C to 20°C. His measurements differ from both the I.S.T. and the A.P.I. 44 tables, the difference increasing with increasing temperature, and being outside the I.S.T. tolerances at the higher temperatures of his range.

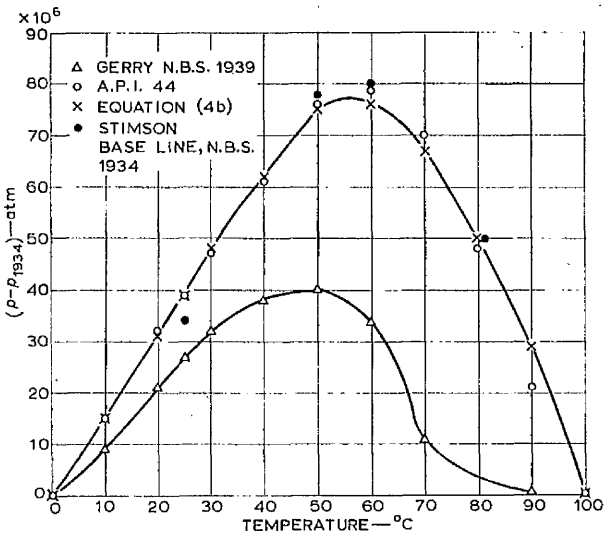


Fig. 4. *Deviations of equation (4b), I.S.T. 1963 values and A.P.I. 44 correlation from 1934 N.B.S. correlation*

The authors decided there were reasonable grounds for preferring the A.P.I. 44 values since the equations of Gerry and Osborne and Meyers do not merge well at temperatures just below 100°C. Further, the measurements of Moser and Zmaczynski (**19**) between 73°C and 130°C are almost identical with the original P.T.R. (**9**) (**10**) observations and the correlation of Osborne and Meyers. Accordingly it was decided to use the A.P.I. 44 values as 'input data' between 0°C and 100°C and the Osborne and Meyers correlation as input data from 100°C to 374·15°C and to fit a single equation to the two sets of data. The basic equation has the same form as equation (4a) and a complementary equation (5b) is similar to (5a). The two sets of equations give virtually the same results except in the range 0°C to 100°C where the second set give slightly higher pressures than the first set. The coefficients for equations (4b) and (5b) are set out in Appendix 1 and Fig. 4 gives deviations of equation (4b) from the 1934 correlation of Osborne and Meyers as well as other pertinent differences. There is good agreement between A.P.I. 44 and the Cragoe–Stimson values except at 25°C where there is an unexplained difference of 4×10^{-6} bar, which may be due to 'smoothing' done originally by Meyers. Equation (4b) agrees with A.P.I. 44 to within 3×10^{-6} bar except at 90°C where the discrepancy is 8×10^{-6} bar. As can be seen both the A.P.I. 44 correlation and equation (4b) give smooth curves whereas the 1939 N.B.S. equation of Gerry appears to be imperfect between 70°C and 100°C, thus demonstrating the poor merging of the two N.B.S. (1939) equations, referred to above and also shown in Figs 2 and 3.

The authors decided not to attempt to improve the equation further since the values obtained were accurate enough for practical purposes and well within the limits of all except the most precise pressure measurements. It was also decided to recommend the use of equations (4b) and (5b) in preference to equations (4a) and (5a), although the latter reproduce the 1963 I.S.T. almost exactly, while at the same time equations (4b) and (5b) give values within the bounds imposed by the tolerances and are equally valid. At temperatures above 100°C both sets of equations give values which are indistinguishable.

SPECIFIC VOLUME OF SATURATED WATER IN THE LIQUID PHASE

As in the preceding section it was again found convenient to use the entries in the N.E.L. Steam Tables as input data. The N.E.L. values, in exact agreement with the I.S.T. values, are derived directly from the N.B.S. table, which in turn is based on the observations of Chappuis (**20**), Thiessen (**21**) and Smith and Keyes (**22**). The experimenters at the N.B.S. found that the observations of Smith and Keyes were not in agreement with their own calorimetric observations above a temperature of 330°C. In order to confirm the reliability of their own experimental measurements Osborne, Stimson and Ginnings carried out special volumetric observations in the neighbourhood of 370°C and consequently computed liquid volume values above 330°C from their own calorimetric observations.

The equation for the specific volume is in the form of a Chebyshev series:

$$\frac{1}{\chi} = \sum_{r=0}^{10}{}' c_r T_r(z) \qquad . \; . \; . \qquad (6)$$

where $$z = 1-2\left(1-\frac{t}{t_{c1}}\right)^{0\cdot4}$$

The volume is expressed in the dimensionless form $\chi = v/v_{c1}$, where v_{c1} is the constant quality described in Appendix 2. In order to achieve thermodynamic consistency between the various equations presented here it was found necessary to accept a slightly lower value for the critical volume than that adopted by the 1963 Steam Conference. The value found by the authors is 3·15 cm³/g as against the Skeleton Table value of 3·17 cm³/g. Further discussion of property values at and in the vicinity of the critical point is given in the concluding section of this paper.

Fig. 5 shows the deviations of the N.B.S. recommended values from equation (6). It was found appropriate to

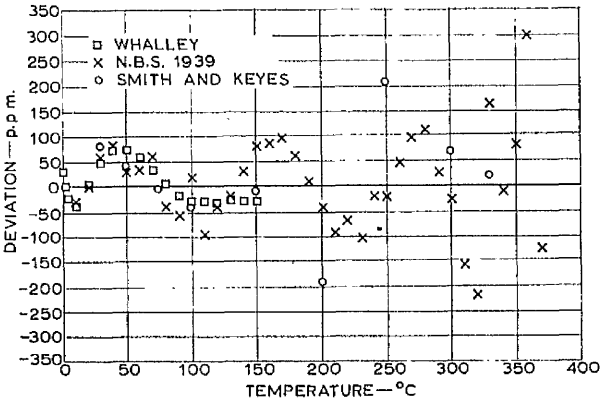


Fig. 5. *Deviation of liquid volume values from equation (6)*

include values derived from the recent data of Whalley (**23**) which extend over the temperature range 0°C to 150°C. In this case Whalley's general correlating equation was used in conjunction with the vapour pressure equation (4a) given here. The results, as can be seen from Fig. 5, are in good agreement with equation (6).

CORRELATION OF THE N.B.S. α VALUES

The α observations are the most important of the N.B.S. calorimetric observations and may be considered second only to the pressure–temperature relation for the saturation line which is fundamental. In deriving the saturation properties it seemed preferable to follow the procedure laid down by Osborne. Accordingly it was decided to refit the α measurements over the whole temperature range replacing the two N.B.S. equations with a single equation. This equation has the form

$$\frac{\alpha}{p_{c1}v_{c1}} = \sum_{r=0}^{11}{}' d_r T_r(q) \quad . \quad . \quad . \quad (7)$$

where $$q = \left\{2\left(\frac{1}{\theta} - 0{\cdot}99\right)^{0{\cdot}5} - E\right\}\Big/ F$$

Fig. 6 shows the deviations of the N.B.S. fitted values from the values given by equation (7). Agreement is maintained to better than 20 p.p.m. except in a very small range of temperature below 10°C, and the values given

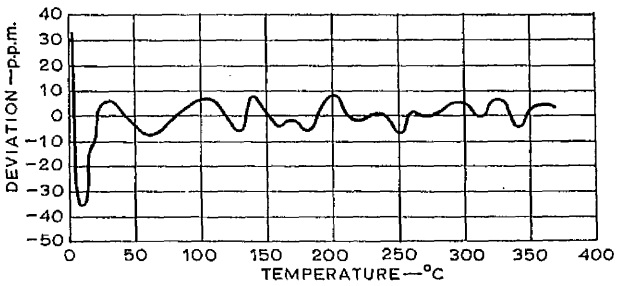


Fig. 6. *Deviation of N.B.S. fitted α values from equation (7)*

Table 4

t, °C	p, bar	$T(\mathrm{d}p/\mathrm{d}T)$, J/cm³	α, J/g	β', J/g	γ, J/g
0	0·006 107	0·012 140 4	−0·000 7	0·012 1	2500·79
0·01	0·006 111	0·012 148 6	0·041 5	0·012 2	2500·76
10	0·012 277	0·023 291 4	42·025 6	0·023 3	2477·12
20	0·023 378	0·042 437 1	83·871 5	0·042 5	2453·65
30	0·042 433	0·073 815 4	125·640 4	0·074 1	2430·10
40	0·073 774	0·123 140 7	167·378 4	0·124 1	2406·34
50	0·123 383	0·197 830	209·104 1	0·200 2	2382·36
60	0·199 24	0·307 192	250·824 4	0·312 4	2358·15
70	0·311 66	0·462 562	292·542 3	0·473 1	2333·67
80	0·473 64	0·677 377	334·259 3	0·697 0	2308·88
90	0·701 12	0·967 195	375·976 9	1·002 0	2283·71
100	1·013 25	1·349 654	417·696 0	1·408 3	2258·10
110	1·432 6	1·844 4	459·42	1·94	2231·95
120	1·985 3	2·472 9	501·14	2·62	2205·18
130	2·701 1	3·258 4	542·86	3·49	2177·70
140	3·613 5	4·225 7	584·58	4·56	2149·43
150	4·759 7	5·400 9	626·30	5·89	2120·27
160	6·180 5	6·811 7	668·00	7·51	2090·13
170	7·920 3	8·486 4	709·69	9·46	2058·94
180	10·027 1	10·454 8	751·36	11·79	2026·60
190	12·552 3	12·747	792·99	14·55	1993·03
200	15·550 5	15·395	834·59	17·81	1958·11
210	19·080	18·431	876·15	21·61	1921·75
220	23·201	21·889	917·66	26·05	1883·82
230	27·979	25·802	959·12	31·19	1844·19
240	33·480	30·207	1000·52	37·13	1802·71
250	39·776	35·142	1041·86	43·97	1759·19
260	46·940	40·649	1083·13	51·85	1713·41
270	55·051	46·773	1124·33	60·91	1665·11
280	64·192	53·565	1165·46	71·35	1613·97
290	74·449	61·080	1206·51	83·40	1559·60
300	85·916	69·386	1247·49	97·39	1501·45
310	98·696	78·560	1288·39	113·73	1438·84
320	112·90	88·694	1329·21	133·00	1370·77
330	128·65	99·912	1369·95	156·04	1295·75
340	146·08	112·39	1410·61	184·20	1211·32
350	165·37	126·40	1451·18	220·05	1112·84
360	186·74	142·51	1491·66	269·84	989·51
370	210·53	161·85	1532·07	360·15	798·71
371	213·06	164·03	1536·10	376·17	768·50
372	215·62	166·27	1540·14	395·97	732·39
373	218·21	168·56	1544·17	422·94	685·20
374	220·84	170·92	1548·20	478·54	598·69
374·15	221·23	171·28	1548·81	539·1	539·1

by equation (7) are well within the accuracy of the original observations.

FORMULATION OF β' VALUES

The quantity β' defined by $v_f T(\mathrm{d}p/\mathrm{d}T)$ can now be formed, using equation (6) for v_f and equation (4b) to derive $\mathrm{d}p/\mathrm{d}T$. The resulting values are given in Table 4. It is found that the resulting agreement, to within 0·2 per cent, is more than adequate, as can also be seen from the tables of derived properties.

FORMULATION OF γ VALUES

The quantities p, v_f and α, each expressed as a function of temperature suffice to calculate all the saturated liquid properties. Further, all the vapour properties can be deduced if γ is now expressed as a function of temperature. This, in fact, was the procedure used by the N.B.S. in generating their table of properties and was the only valid procedure since γ was an observed quantity. However, it has proved more convenient to fit h_g as a function of temperature and to compare the calculated values of γ with the observed values of the N.B.S. This course was dictated by the fact that a complete table of h_g values was ready to hand in the N.E.L. tables, whereas it would be necessary to generate values of γ from the N.B.S. data. Moreover, in view of further work on equations of state planned by the authors it was recognized that it would be more convenient to have h_g as a function of T rather than γ or h_{fg}. It is to be appreciated that only one of these properties need be defined since the other two can then be evaluated.

The following series gives h_g as a function of temperature in the form

$$\frac{1}{\epsilon} = \sum_{r=0}^{10}{}' e_r T_r(w) \quad . \quad . \quad . \quad . \quad (8)$$

where $$w = 1 - G\left(\frac{1}{\theta} - 1\right)^{0\cdot4}$$

and $$\frac{1}{\epsilon} = \frac{p_{c1} v_{c1}}{h_g}$$

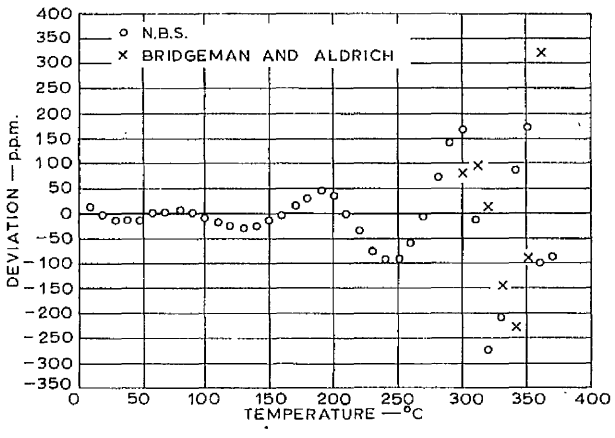


Fig. 7. *Deviation of N.B.S. γ observations from computed values*

Since $h_g = \alpha + \gamma$, γ is immediately derived. In fitting h_g it was found necessary to adopt a value of $h_f = h_g = 2088$ J/g at the critical point in order to achieve thermodynamic consistency. Fig. 7 shows a comparison between the computed γ values and the original N.B.S. observations. Agreement is well within the limits of uncertainty associated with the experimental observations and the procedure for reformulating the γ values is justified.

CALCULATION OF THE ENTRIES IN TABLES 4 AND 5

The argument is temperature and the tabulated values were calculated as follows, in accordance with the resumé given in Appendix 3.

Quantity	*Equation*	*Formula*
p	(4b)	
v_f	(6)	
β'	(4b) and (6)	$\beta' = v_f T \dfrac{\mathrm{d}p}{\mathrm{d}T}$
α	(7)	
h_f	(9)	$h_f = \alpha + \beta'$
s_f	(15)	$s_f = \left[\dfrac{h_f}{T}\right]_{T_t}^{T} + \displaystyle\int_{T_t}^{T} \frac{\alpha}{T^2}\,\mathrm{d}T + c$
h_g	(8)	
γ	(8a)	$\gamma = h_g - \alpha$
h_{fg}	(10)	$h_g - h_f$
v_g	(18)	$v_g = \gamma/T \dfrac{\mathrm{d}p}{\mathrm{d}T}$
s_g	(17)	$[s_g]_{T_t}^{T} = [s_f]_{T_t}^{T} + \left[\dfrac{h_{fg}}{T}\right]_T$

SUMMARY

So far as the authors are aware no new calorimetric experiments similar to those carried out by the N.B.S. have been carried out since 1939. However, there have been additional vapour pressure measurements among which should be included those of Eck (**24**), Moser and Zmaczynski (**19**) and Stimson (**17**). The observations of Eck, who also determined the critical volume, were included by Dorsey (**25**) in his comprehensive survey, the N.B.S. values being preferred. Moser and Zmaczynski obtained complete agreement with the correlation of Osborne and Meyers (N.B.S.) in the temperature range 73°C to 130°C. The unpublished measurements of vapour pressure at 25, 40, 50, 60 and 80°C by Stimson are referred to by Rossini (**26**) in the calibration of apparatus used to determine the boiling points and vapour pressures of petroleum products. They have also been used to provide reference values of the vapour pressures and boiling points of water in the American Petroleum Institute Research Project 44 (16). However, the difference between the A.P.I. 44 value and the original Osborne and Meyers correlation does not exceed 75×10^{-6} atm, an

Table 5

t, °C	p, bar	v_f, cm³/g	v_g, cm³/g	h_f, J/g	h_{fg}, J/g	h_g, J/g	s_f, J/g degK	s_{fg}, J/g degK	s_g, J/g degK
0	0·006 107	1·000 18	205 989	−0·041 6	2500·8	2500·8	−0·0002	9·155	9·155
0·01	0·006 111	1·000 18	205 843	0·000 631	2500·8	2500·8	0·0000	9·155	9·155
10	0·012 277	1·000 39	106 353	42·00	2477·1	2519·1	0·1510	8·748	8·899
20	0·023 378	1·001 8	57 819	83·86	2453·7	2537·5	0·2963	8·370	8·666
30	0·042 433	1·004 4	32 921	125·66	2430·1	2555·7	0·4365	8·016	8·452
40	0·073 774	1·007 8	19 541	167·45	2406·3	2573·7	0·5721	7·684	8·256
50	0·123 383	1·012 1	12 042	209·25	2382·2	2591·5	0·7035	7·372	8·075
60	0·199 24	1·017 1	7 676·5	251·08	2357·9	2609·0	0·8310	7·077	7·908
70	0·311 66	1·022 7	5 045·1	292·96	2333·2	2626·2	0·9548	6·799	7·754
80	0·473 64	1·029 0	3 408·6	334·90	2308·2	2643·1	1·0753	6·536	7·611
90	0·701 12	1·036 0	2 361·2	376·93	2282·8	2659·7	1·1925	6·286	7·478
100	1·013 25	1·043 5	1 673·1	419·05	2256·7	2675·8	1·3069	6·048	7·355
110	1·432 6	1·051 6	1 210·1	461·30	2230·1	2691·4	1·4185	5·820	7·239
120	1·985 3	1·060 3	891·74	503·7	2202·6	2706·3	1·528	5·602	7·130
130	2·701 1	1·069 7	668·34	546·3	2174·3	2720·6	1·634	5·393	7·027
140	3·613 5	1·079 8	508·66	589·1	2144·9	2734·0	1·739	5·191	6·931
150	4·759 7	1·090 5	392·57	632·1	2114·4	2746·6	1·842	4·997	6·838
160	6·180 5	1·102 0	306·85	675·5	2082·7	2758·1	1·942	4·808	6·751
170	7·920 3	1·114 3	242·62	719·1	2409·5	2768·6	2·042	4·625	6·666
180	10·027 1	1·127 4	193·84	763·1	2014·9	2778·0	2·139	4·446	6·586
190	12·552 3	1·141 5	156·35	807·5	1978·5	1786·0	2·236	4·272	6·507
200	15·550 5	1·156 5	127·19	852·3	1940·4	2792·7	2·331	4·101	6·431
210	19·080	1·172 7	104·265	897·7	1900·2	2977·9	2·425	3·933	6·358
220	23·201	1·190 1	86·064	943·7	1857·8	2801·5	2·518	3·767	6·285
230	27·979	1·208 8	71·476	990·3	1813·1	2803·3	2·610	3·603	6·214
240	33·480	1·229 1	59·679	1037·6	1765·6	2803·2	2·702	3·441	6·143
250	39·776	1·251 2	50·059	1085·8	1715·3	2801·0	2·794	3·279	6·072
260	46·940	1·275 4	42·151	1134·9	1661·6	2796·5	2·885	3·116	6·001
270	55·051	1·302 2	35·600	1185·2	1604·3	2789·4	2·976	2·954	5·980
280	64·192	1·332 0	30·131	1236·8	1542·7	2779·4	3·068	2·789	5·857
290	74·449	1·365 5	25·533	1289·9	1476·2	2766·1	3·161	2·621	5·782
300	85·916	1·403 6	21·639	1344·8	1404·1	2748·9	3·255	2·450	5·705
310	98·696	1·447 7	18·315	1402·1	1325·2	2727·2	3·351	2·272	5·623
320	112·90	1·499 5	15·455	1462·2	1237·8	2700·0	3·449	2·087	5·536
330	128·65	1·561 7	12·969	1525·9	1139·8	2665·7	3·552	1·890	5·442
340	146·08	1·639 0	10·778	1594·8	1027·2	2621·9	3·660	1·675	5·336
350	165·37	1·741	8·804	1671·2	892·8	2564·0	3·779	1·433	5·212
360	186·74	1·893	6·943	1761·5	719·7	2481·2	3·916	1·137	5·053
370	210·53	2·225	4·935	1892·2	438·6	2330·8	4·113	0·682	4·795
371	213·06	2·293	4·685	1912·2	392·4	2304·6	4·144	0·609	4·753
372	215·62	2·38	4·40	1936·1	336·5	2272·5	4·180	0·521	4·701
373	218·21	2·51	4·06	1967·1	262·3	2229·4	4·227	0·406	4·633
374	220·84	2·80	3·50	2026·7	120·2	2146·9	4·318	0·186	4·504
374·15	221·23	3·15	3·15	2087·9	−0·0	2087·9	4·412	−0·000	4·412

amount small enough to keep the A.P.I. 44 values within the I.S.T. tolerances. There are also measurements in the range 0°C to 20°C by Douslin (**18**) which do not agree with any of the above references and show an error, with respect to the I.S.T., increasing with temperature and outside the tolerance. Since Douslin's observations are as yet unsupported by corroborating work the only change justified would be towards the A.P.I. 44 values and this the authors have done.

Apart from the low temperature vapour pressures which may be in error by a very small amount the only other region where there is some doubt is around the critical point. It is inevitable that a fairly large uncertainty must be associated with the values of the properties at the critical point. It is clear that the value of the critical volume ($v_{c1} = 3{\cdot}17$ cm³/g) selected by the Sixth I.C.P.S. is too high. The authors found, using the method of rectilinear diameters, a value of 3·11 cm³/g accepting the N.B.S. liquid and vapour volumes. Bridgeman and Aldrich (**27**), using a special procedure, reanalysed the N.B.S. calorimetric measurements and obtained a value of 3·1547 cm³/g at 374·02°C. They also took into consideration differences

Table 6. *p, v, T values at the critical point*

	Pressure, bar	Volume, cm³/g	Temperature, °C (I.P.T.S.)
1963 I.S.T.	221·2 ±0·1	3·17 ±0·15	374·15 ±0·10
Bridgeman and Aldrich (**27**)	222·261	3·1547	374·02 374·136 °C (therm)
Rivkin (**28**)		3·165 ±0·019	
Juza (**29**) (best values)	221·06	3·16	374·07
Present work	221·23	3·15	374·15

between the temperature scales. Their findings are best summarized in Table 6 along with the estimates of recent workers. The most recent analysis is that of Juza (**29**) who suggests that further experimental and theoretical work is needed to reduce the uncertainties on the various properties at the critical point.

CONCLUSION

The authors believe that their equations adequately specify the thermodynamic properties of saturated liquid and vapour water substance. The only area where any large measure of disagreement exists is in the vicinity of the critical point.

ACKNOWLEDGEMENTS

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They wish to thank also a number of colleagues who have assisted in preparing this work.

APPENDIX 1

SUMMARY OF EQUATIONS AND COEFFICIENTS

Equations

Vapour pressure of saturated water (basic equation)

$$\ln \beta = \sum_{r=0}^{n}{}' a_r T_r(x) \quad . \quad . \quad \text{(4a) and (4b)}$$

where $x = \left\{2\left(\frac{1}{\theta}-0{\cdot}95\right)^{0{\cdot}4} - A\right\}\Big/B,$

$n = 11$ in (4a),

$n = 12$ in (4b).

Vapour pressure of saturated water (supplementary equation)

$$\frac{1}{\theta} = \sum_{r=0}^{11}{}' b_r T_r(y) \quad . \quad . \quad \text{(5a) and (5b)}$$

where $y = \left\{2\left[\ln\left(\frac{1{\cdot}1}{\beta}\right)\right]^{0{\cdot}4} - C\right\}\Big/D.$

Specific volume of saturated liquid

$$\frac{1}{X} = \sum_{r=0}^{10}{}' c_r T_r(z) \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where $z = 1-2\left(1-\frac{t}{t_{c1}}\right)^{0{\cdot}4}.$

The following weighting factors were applied to the volumes used as input data:

20 at 0°C, 0·01°C and 1°C

10 from 2°C to 10°C inclusive

Coefficients

Equation (4a)

a_0	$-8{\cdot}119\,364\,2$	a_6	$5{\cdot}362\,281\,8\times10^{-4}$
a_1	$5{\cdot}132\,255\,5$	a_7	$1{\cdot}245\,539\,9\times10^{-4}$
a_2	$-1{\cdot}184\,240\,7$	a_8	$-4{\cdot}915\,428\,8\times10^{-5}$
a_3	$1{\cdot}177\,959\,2\times10^{-1}$	a_9	$4{\cdot}630\,256\,5\times10^{-5}$
a_4	$-5{\cdot}157\,642\,0\times10^{-3}$	a_{10}	$1{\cdot}530\,133\,4\times10^{-5}$
a_5	$-1{\cdot}468\,953\,7\times10^{-3}$	a_{11}	$-2{\cdot}095\,453\,0\times10^{-5}$
A	$1{\cdot}452\,207\,17$	B	$-0{\cdot}848\,789\,53$

Equation (4b)

a_0	$-8{\cdot}119\,182\,2$	a_6	$4{\cdot}709\,130\,0\times10^{-4}$
a_1	$5{\cdot}132\,102\,1$	a_7	$1{\cdot}623\,639\,8\times10^{-4}$
a_2	$-1{\cdot}184\,166\,9$	a_8	$-7{\cdot}168\,068\,8\times10^{-5}$
a_3	$1{\cdot}178\,099\,3\times10^{-1}$	a_9	$7{\cdot}011\,612\,7\times10^{-5}$
a_4	$-5{\cdot}229\,133\,9\times10^{-3}$	a_{10}	$-1{\cdot}336\,948\,0\times10^{-5}$
a_5	$-1{\cdot}382\,926\,0\times10^{-3}$	a_{11}	$7{\cdot}262\,101\,3\times10^{-6}$
A	$1{\cdot}452\,207\,17$	a_{12}	$-1{\cdot}241\,383\,3\times10^{-5}$
		B	$-0{\cdot}848\,789\,53$

Equation (5a)

b_0	$3{\cdot}045\,293\,7$	b_6	$6{\cdot}841\,155\,4\times10^{-5}$
b_1	$-6{\cdot}823\,095\,2\times10^{-1}$	b_7	$3{\cdot}365\,000\,7\times10^{-5}$
b_2	$1{\cdot}641\,149\,5\times10^{-1}$	b_8	$-1{\cdot}234\,224\,8\times10^{-5}$
b_3	$-2{\cdot}023\,216\,5\times10^{-3}$	b_9	$1{\cdot}482\,655\,0\times10^{-6}$
b_4	$-1{\cdot}923\,911\,1\times10^{-3}$	b_{10}	$-1{\cdot}021\,164\,5\times10^{-6}$
b_5	$-5{\cdot}745\,494\,2\times10^{-4}$	b_{11}	$-4{\cdot}090\,809\,0\times10^{-6}$
C	$2{\cdot}960\,942\,5$	D	$-2{\cdot}179\,888\,01$

Equation (5b)

b_0	$3{\cdot}045\,315\,5$	b_6	$6{\cdot}057\,986\,6\times10^{-5}$
b_1	$-6{\cdot}823\,282\,2\times10^{-1}$	b_7	$3{\cdot}839\,585\,0\times10^{-5}$
b_2	$1{\cdot}641\,239\,5\times10^{-1}$	b_8	$-1{\cdot}449\,978\,5\times10^{-5}$
b_3	$-2{\cdot}021\,829\,2\times10^{-3}$	b_9	$4{\cdot}360\,822\,0\times10^{-6}$
b_4	$-1{\cdot}932\,334\,1\times10^{-3}$	b_{10}	$-3{\cdot}058\,546\,3\times10^{-6}$
b_5	$-5{\cdot}642\,725\,4\times10^{-4}$	b_{11}	$-6{\cdot}057\,498\,7\times10^{-7}$
C	$2{\cdot}960\,942\,50$	D	$-2{\cdot}179\,888\,01$

c_0	$4{\cdot}332\,053$	c_6	$-3{\cdot}765\,370\times10^{-3}$
c_1	$-1{\cdot}107\,796$	c_7	$1{\cdot}123\,345\times10^{-3}$
c_2	$-5{\cdot}275\,102\times10^{-2}$	c_8	$-2{\cdot}458\,266\times10^{-3}$
c_3	$2{\cdot}173\,547\times10^{-2}$	c_9	$-1{\cdot}425\,530\times10^{-3}$
c_4	$-1{\cdot}754\,636\times10^{-2}$	c_{10}	$-1{\cdot}304\,721\times10^{-3}$
c_5	$5{\cdot}125\,009\times10^{-3}$		

Equations	*Coefficients*

Saturated liquid α equation

$$\frac{\alpha}{p_{c1}v_{c1}} = \sum_{r=0}^{11}{}' d_r T_r(q) \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where $q = \left\{2\left(\frac{1}{\theta}-0{\cdot}99\right)^{0{\cdot}5} - E\right\}\Big/ F.$

The following weighting factors were applied to the α values used as input data:

5 from 356°C to 370°C inclusive

26 from 371°C to 374·15°C inclusive

$d_0 =$	$2{\cdot}262\,821$	$d_6 =$	$6{\cdot}365\,584\times10^{-4}$
$d_1 =$	$1{\cdot}164\,542$	$d_7 =$	$8{\cdot}949\,914\times10^{-5}$
$d_2 =$	$-1{\cdot}529\,470\times10^{-2}$	$d_8 =$	$-2{\cdot}309\,905\times10^{-5}$
$d_3 =$	$-6{\cdot}087\,624\times10^{-2}$	$d_9 =$	$1{\cdot}352\,658\times10^{-5}$
$d_4 =$	$-1{\cdot}233\,320\times10^{-2}$	$d_{10} =$	$-5{\cdot}909\,329\times10^{-6}$
$d_5 =$	$6{\cdot}246\,461\times10^{-4}$	$d_{11} =$	$-2{\cdot}335\,760\times10^{-6}$
$E =$	$1{\cdot}274\,631\,9$	$F =$	$-1{\cdot}074\,631\,9$

Specific enthalpy of saturated vapour

$$\frac{1}{\epsilon} = \sum_{r=0}^{10}{}' e_r T_r(w) \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where $w = 1-G\left(\frac{1}{\theta}-1\right)^{0{\cdot}4}$.

$e_0 =$	$5{\cdot}600\,998\times10^{-1}$	$e_6 =$	$-1{\cdot}394\,169\times10^{-4}$
$e_1 =$	$2{\cdot}298\,094\times10^{-2}$	$e_7 =$	$-1{\cdot}841\,311\times10^{-4}$
$e_2 =$	$2{\cdot}908\,374\times10^{-2}$	$e_8 =$	$-1{\cdot}087\,239\times10^{-4}$
$e_3 =$	$5{\cdot}286\,767\times10^{-3}$	$e_9 =$	$-4{\cdot}918\,106\times10^{-5}$
$e_4 =$	$-7{\cdot}390\,192\times10^{-4}$	$e_{10} =$	$-2{\cdot}310\,695\times10^{-5}$
$e_5 =$	$-3{\cdot}042\,949\times10^{-4}$	$G =$	$1{\cdot}763\,487$

Chebyshev polynomial

The function $T_r(x)$ is the Chebyshev polynomial (or T-polynomial) of rth degree with x normalized in the range $-1 \leqslant x \leqslant 1$. The first two T-polynomials are

$$T_0(x) = 1 \quad \text{and} \quad T_1(x) = x$$

The remaining T-polynomials are calculated using the recurrence relation

$$T_n(x) = 2xT_{(n-1)}(x) - T_{(n-2)}(x)$$

Hence $\quad T_2(x) = 2x^2-1; \quad T_3(x) = 4x^3-3x; \quad$ etc.

Derivatives

In a set of Chebyshev coefficients, a_r, of the polynomial

$$y = \sum_{r=0}^{n}{}' a_r T_r(x) \quad . \quad . \quad . \quad . \quad . \quad (i)$$

the prime indicates that the first term of the sum is to be halved.

On differentiating y with respect to x in equation (i) we obtain

$$\frac{dy}{dx} = \sum_{r=0}^{n-1}{}' A_r T_r(x) \quad . \quad . \quad . \quad . \quad . \quad (ii)$$

where $\quad A_{r-1} = A_{r+1} + 2ra_r$

and $\quad A_n = A_{n+1} = 0$

A description of Chebyshev polynomials is given in Chapter 8 of *Modern computing methods*, 2nd edition (*N.P.L. Notes on Applied Science*, No. 16, H.M.S.O., 1961).

APPENDIX 2

Reduced dimensionless quantities

$p/p_{c1} = \beta$, reduced pressure

$T/T_{c1} = \theta$, reduced temperature

$v/v_{c1} = \chi$, reduced volume

$h/(p_{c1}v_{c1}) = \epsilon$, reduced enthalpy

Defined constant quantities (1966 Formulation)

$s_{ft} = 0, \; u_{ft} = 0$

$p_{t1} = 611{\cdot}2 \text{ N/m}^2 = 611{\cdot}2 \text{ J/m}^3$

$T_{c1} = 647{\cdot}3°\text{K}$

$p_{c1} = 22\,120\,000 \text{ N/m}^2 = 22\,120\,000 \text{ J/m}^3$

$v_{c1} = 0{\cdot}003\,17 \text{ m}^3\text{/kg} = 3{\cdot}17 \text{ cm}^3\text{/g}$

$R_1 = 461{\cdot}51 \text{ J/kg degK}$

$1 \text{ bar} = 10^5 \text{ N/m}^2$

APPENDIX 3

RESUMÉ OF THERMODYNAMIC EXPRESSIONS REQUIRED TO FORMULATE THE SATURATION PROPERTIES

By definition from Osborne we have

$$\alpha = h_f - Tv_f \frac{dp}{dT} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\beta' = v_f T \frac{dp}{dT} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and

$$\gamma = v_g T \frac{dp}{dT} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where α, β' and γ represent the N.B.S. basic observations.

We may combine these equations to give

$$h_f = \alpha + \beta' \quad . \quad . \quad . \quad . \quad . \quad (9)$$

and

$$h_g = \alpha + \gamma \quad . \quad . \quad . \quad . \quad . \quad (8a)$$

also

$$h_{fg} = \gamma - \beta' \quad . \quad . \quad . \quad . \quad . \quad (10)$$

since $\frac{h_{fg}}{v_{fg}} = T\frac{dp}{dT}$ which is the Clapeyron–Clausius equation.

Integration of equation (9) gives the enthalpy of the saturated liquid at any temperature T with respect to a datum at T_0.

Hence

$$[h_f]_{T_t}^{T} = \int_{T_t}^{T} \alpha \, dT + \int_{T_t}^{T} v_f T \frac{dp}{dT} dT \quad . \quad . \quad (11)$$

$$= \int_{T_t}^{T} \alpha \, dT + \int_{T_t}^{T} \beta' \, dT \quad . \quad . \quad . \quad (12)$$

Now $\quad dh = T\,ds + v\,dp$

or $\quad ds = \frac{dh}{T} - \frac{v}{T}dp$

and since $\quad \frac{dh}{T} = d\left(\frac{h}{T}\right) + \frac{h}{T^2}dT$

$$ds = d\left(\frac{h}{T}\right) + \frac{h}{T^2}dT - \frac{v}{T}dp$$

If we apply this equation to the saturated liquid we may write

$$ds_f = d\left(\frac{h_f}{T}\right) + \frac{h_f}{T^2}dT - \frac{v_f}{T}dp \quad . \quad . \quad (13)$$

Equation (13) may be reduced using equation (1) and we get

$$ds_f = d\left(\frac{h_f}{T}\right) + \frac{\alpha}{T^2}dT \quad . \quad . \quad . \quad . \quad (14)$$

Integration of equation (14) gives the entropy of the saturated liquid as

$$[s_f]_{T_t}^{T} = \left[\frac{h_f}{T}\right]_{T_t}^{T} + \int_{T_t}^{T} \frac{\alpha}{T^2}\,\mathrm{d}T + c \quad . \quad . \quad . \quad (15)$$

where c is a constant of integration depending on the datum state. For the saturated vapour

$$[h_g]_{T_t}^{T} = [h_f]_{T_t}^{T} + [h_{fg}]_T \quad . \quad . \quad . \quad . \quad (16)$$

$$[s_g]_{T_t}^{T} = [s_f]_{T_t}^{T} + \left[\frac{h_{fg}}{T}\right]_T \quad . \quad . \quad . \quad (17)$$

and

$$v_g = \frac{\gamma}{T\dfrac{\mathrm{d}p}{\mathrm{d}T}} \quad . \quad . \quad . \quad . \quad . \quad (18)$$

APPENDIX 4

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An Equation of State for Compressed Water from 1 to 1000 bar and from 0 °C to 150 °C

by

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Notation

a, b, c, d		Coefficients
c_p	J/g K	Specific heat capacity
c_p^o	J/g K	Specific heat capacity at zero pressure
$f = u - Ts$	J/g	Specific free energy (Helmholtz function)
$g = h - Ts$	J/g	Specific free enthalpy (Gibb's function)
g'	m/s^2	Acceleration due to gravity
$h = u + pv$	J/g	Specific enthalpy
$p(p_1, p_2, p_p)$	bar	Pressure
s	J/g K	Specific entropy
t	^oC	Temperature
T	^oK	Temperature
$T_i(x)$		Chebyshev polynomial
u	J/g	Specific internal energy
v	cm^3/g	Specific volume
v_A	cm^3/g	Specific volume at one atmosphere (p_A)
V	m/s	Velocity
$x = \frac{2s - 11.99}{12.01}$		Normalised entropy
$y = \frac{2p - 1000}{1000}$		Normalised pressure
z	m	Height above datum

Subscripts

f	Refers to saturated liquid state
t, c	Refer to the states at triple and critical points respectively

An Equation of State for Compressed Water from 1 to 1000 bar and from 0 °C to 150 °C

by M. R. Gibson* and E. A. Bruges†

Abstract

The precision with which the thermodynamic properties of compressed water and steam are known has led, not unnaturally, to the development of equations of state suitable only for use on electronic digital computers. The equations are in the main empirical although some are highly sophisticated and lead to lengthy programmes and complex sub-routines. Among such equations are those of the 1966 and 1967 Formulations of the Thermodynamic Properties of Ordinary Water Substance prepared by the International Formulation Committee (1) of the International Steam Conference. The favoured form of equation has been one in which the dependent variables are enthalpy, volume and entropy and the independent variables pressure and temperature. However, this form of equation may not prove to be always the most suitable and the purpose of this paper is to describe how another type of equation, in which the dependent variable is enthalpy and the independent variables are pressure and entropy, may be established and applied. It is believed that this particular type of equation, relating as it does the three most important parameters in pump and turbine performance, has special qualities for design and efficiency calculations. By way of example the efficiency of a water turbine is evaluated according to the 'thermodynamic method' described by Thom (2). A concluding section outlines the further steps being taken by the authors to provide a similar type of equation over ranges of pressure and temperature up to 1000 bar and 1000 °C.

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Introduction

In an address to the Sixth International Conference on the Properties of Steam, New York 1963, R. W. Bain (3) suggested that it might be possible to cover the entire liquid and vapour regions with a single equation of the form $h = h(p,s)$ - other forms are $p = p(h,s)$ and $s = s(h,p)$. This is one of four canonical equations

$$u = u(s,v) \quad \text{_____(1)}$$

$$f = f(v,T) \quad \text{_____(2)}$$

$$g = g(T,p) \quad \text{_____(3)}$$

$$\text{and } h = h(p,s) \quad \text{_____(4)},$$

which possess a number of advantages over those in which the various properties (h, v, s etc) are expressed as functions of p and T. If $p = p(v, T)$ _____(5) not only is it unlikely that a single equation can cover both the liquid and vapour phases but additional information has to be supplied in order that energy quantities may be calculated. This is usually expressed as $c_p^{\circ} = f(T)$___(6).

Formulations, comprising equations (5) and (6) for example, involve both integration and differentiation in computing the usual properties, whereas any one of the canonical equations (1) to (4) defines all thermodynamic properties using only the quantities themselves and their derivatives. The derivation of the various thermodynamic properties from the four canonical equations was demonstrated by Bain and Le Fevre (4) in a paper from which the entries in table 1 have been taken. Columns (1) and (2) of this table give the quantities appropriate to the canonical equations (4) and (2) and column (3) refers to the form $p = p(v,T)$, which is not a canonical form and for which it can be seen that both integration and differentiation are required.

In addition to the computative advantages of the canonical equations derivative quantities across the saturation line are smooth and all quantities are continuous. The absence of gross discontinuities such as are exhibited by an equation of the form $p = p(v,T)$ is a further factor in favour of the surface $h = h(p,s)$, which is represented in figure 1. This particular type of equation seems to have been advanced in the first instance by Holmes and

Hollitch (5) who covered the field of industrial interest with a series of equations for compressed water and steam. Juza (6) has also presented equations of this type specifically for industrial calculations but no attempt to provide a single equation, as suggested by Bain, has yet succeeded. Haywood (7) at the instigation of the U.K. Committee on the Properties of Steam (ERA Research Advisory Committee 2B as it was then termed) made a preliminary investigation which was subsequently followed up by McLeod (8) at the National Engineering Laboratory. Taking the form of the surface as $s = s(p,h)$ and using constraints McLeodwas unable to obtain a surface from which satisfactory properties could be derived. As a contribution to the U.K. effort the authors (9) respecified the saturation properties in terms of equations suitable for computers and, following a computation of the properties of compressed water, moved on to the problem of the h-p-s surface. It is this latter work which is described here and which is believed to supply a valuable clue to any future fitting of this or similar thermodynamic surfaces.

Surface fitting procedure

After successfully using orthogonal Chebyshev polynomials to represent the saturation properties (9), the method, which is now described, was extended to fitting the h-p-s surface. Initially enthalpy is fitted as a function of entropy along isobars in the form

$$h = \sum_{i=0}^{n}{}' a_i T_i(x) \qquad (7)$$

where $x = (2s - 11.99)/12.01$.

(A description of the Chebyshev polynomials, $T_i(x)$, is given in appendix 2). The $(n + 1)$ coefficients obtained from equation (7) were then fitted as functions of pressure in the form

$$a_i = \sum_{j=0}^{m}{}' b_{ij} T_j(y) \qquad (8)$$

$$\text{for } i = 0, 1, 2 \ldots\ldots (n-1), n$$

$$\text{where } y = \frac{2p - 1000}{1000}$$

Equations (7) and (8) may now be combined to give

$$h = \sum_{i=0}^{n}{}' \sum_{j=0}^{m}{}' b_{ij} T_i(x) T_j(y) \qquad (9),$$

which is a representation of the h-p-s surface.

In order to test the computer programs which were written to carry out the above process it was decided to use as input data the values of enthalpy and entropy tabulated in the 1964 NEL Steam Tables (10). Although an adequate fit in enthalpy as a function of entropy was obtained along any isobar the input temperature, T, could not be recovered through the relation $T = \frac{\partial h}{\partial s}_p$. In addition, values of volume, v, derivable through the relation $v = \frac{\partial h}{\partial p}_s$ were quite unsatisfactory. These troubles arose from two sources. As regards reproducing the original input temperature the fault was attributed to "round off" present in the tabulated values of enthalpy and entropy and small thermodynamic inconsistencies in that part of the table relating to compressed water in the range 0 °C to 150 °C. In their study Haywood and Bott (7) warned against the possibility of this troublesome interaction between the smoothing of the table values and the fitting polynomials. Inability to derive satisfactory volume values stemmed from the fact that there was an insufficient number of temperature intervals. The coefficients a, when plotted, were not smooth and it followed that satisfactory values of v could not be obtained. It became clear that although these tables gave satisfactory entries, within the Skeleton Table tolerances, the entries could not be used to provide input data such as would seem necessary for generating the h-p-s surface.

Creation of new input data

At this stage it was decided to set aside the NEL Tables as a source of input data and to generate an entirely new set of values of h and s at such intervals of pressure and temperature as the preliminary surface-fitting work suggested. For this purpose the volume measurements of Kell and Whalley (11), through their correlating equation

$$\frac{v}{v_A} = 1 + \sum_{i=0}^{5} \sum_{j=1}^{3} d_{ij}\, t^i (p - p_A)^j \qquad (10),$$

were used to compute the thermodynamic properties of compressed water. Equation (10) cannot be used without certain additional information relating to v_A and the saturated liquid values. The necessary saturated liquid values were obtained from the authors' earlier publication (9) and values of v_A were derived from an expression established by one of us (MRG) and published by Bruges (12). The expression for v_A is repeated here in appendix 1 for the

convenience of the reader. In this latter publication the volume measurements of Kell and Whalley are compared with those of Amagat (13), Smith and Keyes (14), Kennedy, Knight and Holser (15) and Vukalovich (16). There is little doubt that the data of Kell and Whalley enable the best possible evaluation of the thermodynamic properties of compressed water to be made and the next stage of the work was to repeat the earlier surface-fitting. Since the volumes were given to six significant figures it was decided to calculate all the input data to six significant figures also and to have as many isobars as isotherms.

The values of enthalpy and entropy at intervals of 1 deg.C along the isobars were evaluated from equation (10), using the relationships in column 3 of Table 1. Then by fitting along each isobar using equation (7), the optimum value of n was found to be 4. The coefficients A_i thus obtained were then fitted from eqn.(8) and a value of 3 for m was found to be adequate. The values of the coefficients b_{ij} are now substituted in eqn.(9) to provide the new surface from which it is necessary to reform not only the input data h, p and s, but also T, v and c_p. It is also necessary to make a comparison with the values in the 1963 International Skeleton Tables and their tolerances. It was found that over the whole region covered by the new equation agreement with the input data was extremely good and that the new equation gave values within the IST tolerances except along the 150°C isotherm at pressures below 150 bar and at 0°C and 1 bar. These discrepancies were overcome by a weighting procedure and the final form of eqn. (9), whose coefficients are tabulated in table 2, was obtained.

This final equation meets the criteria laid down by the 1963 IST. At all the skeleton table points the values of enthalpy lie within the tolerances while the values of volume also lie within the tolerance with the exception of the 150°C isotherm from p = 25 bar to p = 125 bar where the values take up all the tolerance. The saturation line provides a boundary to the equation from 100°C to 150°C and a comparison with the IST saturated liquid values is given in table 4. In addition, table 4 gives saturated liquid values from 100°C down to 0°C so that the possibility of using the equation below 1 bar paressure and so extrapolating its range to the saturation line from 0°C to 100°C may be considered. As can be seen from tables 3 and 4, with the exception of the liquid volume values at 0°C and 0.01°C all values are within the prescribed tolerances.

A comparison of the saturation values which may be derived from eqn. (9)

is made in table 5 with the values previously obtained by the authors (9). Included are values of c_{p_f} which are calculated from the equation

$$c_{p_f} = \left(\frac{\partial h}{\partial T}\right)_f - \frac{dp}{dT_f}\left\{v_f - \left(\frac{\partial v}{\partial T}\right)_p T\right\} \quad \text{(11)},$$

where $\left(\frac{\partial v}{\partial T}\right)_p$ is derived from equation (10) and the other quantities from reference (9).

In addition, values derived from equation (9) are compared in figures 2, 3, 4 and 5 with the corresponding values derived from the observations of Kell and Whalley. The comparison is made for the 0, 50, 100 and 150 °C isotherms.

Efficiency of a water turbine

The efficiency of a water turbine or pump may be determined very elegantly by the 'thermodynamic method', a method which depends not only on the thermodynamic properties of water but also on the precision with which small temperature changes can be measured. Evaluation of the thermodynamic properties in such efficiency calculations may be carried out very easily using equation (9) and the following hypothetical results for a turbine are used to illustrate such an application.

The efficiency, η_{tu}, of a turbine is given by

$$\eta_{tu} = \frac{(h_1 - h_2)10^3 + g'(z_1 - z_2) + (V_1^2 - V_2^2)/2}{(h_p - h_2)_{s_p} 10^3 + g'(z_p - z_2) + (V_p^2 - V_2^2)/2} \quad \text{(12)}$$

where the suffices refer to the measuring stations shown in figure 6. In the example shown a small flow of water is taken from a point upstream of the turbine and throttled in a calorimeter. The temperature difference $(T_2 - T_1) = \Delta T$ is measured, from which observation the necessary fluid properties can be deduced. The following constants, table 6, apply to the turbine for which the computed efficiencies are given in table 7.

TABLE 6

g'	9.798 m/s^2
z_1	479.2 m
z_2	476.9 m
z_p	481.8 m
V_1	0.5 m/s
V_2	5.2 m/s
V_p	zero (included in enthalpy term)
p_2	1.1×10^5 N/m^2
p_p	49.20×10^5 N/m^2
$T_1 = T_p = 10^oC$	
$(h_1 - h_2)10^3$	enthalpy change J/kg
$(h_p - h_2)_s 10^3$	isentropic enthalpy change J/kg

TABLE 7

$p_1 \times 10^{-5}$ N/m^2	$\Delta T \times 10^3$ °C	η_{tu} %		
		Thom's method	Eqn.(9)	Eqn.(10)
48.42	50.3	90.90	90.89	90.91
48.65	63.2	90.25	90.23	90.26
48.74	71.9	89.67	89.66	89.68
48.90	72.1	89.97	89.96	89.99
48.95	66.4	90.57	90.56	90.58
48.88	72.8	89.88	89.86	89.89
		Average 90.21	90.19	90.22

The efficiencies so derived are compared with the values which would have been obtained had the primary data, from which equation (9) was itself derived, been used instead. The efficiencies in the first column are derived by using certain coefficients described by Thom (2) where a full account of the 'thermodynamic method' is given. For the sake of completeness a revised

set of coefficients, based on equation (10) is given here although the values differ only marginally from those quoted by Thom.

It is immediately seen from table 7 that equation (9) gives values of η_{tu} in excellent agreement not only with those which may be derived from the primary data of equation (10) but also with the values obtained by Thom's method. The authors would commend equation (9) to the practitioners of the thermodynamic method, of which group Thom is a member, together with the values of the coefficients given in appendix 3. It is believed that considerable advantage would be derived by expressing all the quantities appearing in equation (12) in S.I. units as the authors have done.

Extension of the h-p-s surface to high temperatures

The successful development of equation (9) and its application, as demonstrated in the preceding section, encouraged the authors to believe that even if the whole field up to 1000 bar and 1000 ^{o}C could not be covered by a single equation of the h-p-s variety it seemed reasonably certain that the field could be divided up into a number of sub-regions. Each sub-region would be represented by a suitable equation which more likely than not would match almost exactly with its neighbour along inter-regional boundaries, since it would only be a question of matching like with like. Apart from finding out how to divide up the surface, shown in figure 1, assuming this to be necessary, there is the additional and all important task of providing consistent input data in the form of h and s at close intervals of p and T. Although the NEL Steam Tables had previously been discarded, for reasons already given, equations were provided from which a smooth set of input data could be derived. However, these equations would not take into account the latest specific heat capacity observations of Sirota at the high pressures (between 600 and 1000 atm) and it was decided to examine other sources. The only other sources are the 1966 and 1967 formulations of the I.F.C.(1) and the formulation of Juza (17). Of these the only formulation worth considering is the latter since the 1966 and 1967 IFC formulations exhibit relatively large discontinuities at the inter-regional boundaries and near these

boundaries first differences of enthalpy are easily shown not to be smooth. Previous experience showed smoothness and absence of discontinuities to be essential in the input data if a satisfactory h-p-s surface was to be generated. Consequently, it was decided that Juza's formulation should be used to provide the required input data repeating the fitting of the temperature range $0^{o}C$-$150^{o}C$ if necessary.

Juza's formulation, based on the equation of van der Waals, is one which has taken many years to develop and although its complexity may discourage many a user the authors have successfully checked its quality by evaluating h, v, s and c_p at close intervals and found no discontinuities or irregularities which could make it unacceptable for further surface-fitting work. Juza's formulation covers the fluid from 100,000 bar to 1000 ^{o}C with four regions and it is important to confirm that the functions h, p and s are sufficiently smooth across the three inter-regional boundaries. The adequacy of this formulation is shown in table 8 which gives the discontinuities in p, h and s as dp, dh and ds together with the maximum discontinuities recommended by the IFC which were 0.005 p, 0.2 J/g and 0.0002 J/gK respectively. The only boundary where the recommended values are exceeded is in a range of temperature $255(t_s) \leq t \leq 272\ ^{o}C$.

Conclusion

The authors have established an equation for compressed water of the form h = h(p,s) and have demonstrated its suitability for evaluating the efficiency of water pumps and turbines. They have also shown that consistent input data in the form of values of h, p and s at sufficiently close intervals of temperature and pressure is required to achieve the necessary result. An indication of how the work will now be extended to higher temperatures through the formulation of Juza is given together with a brief appraisal of this formulation. It is believed that an interlocking set of equations may now be derived thus providing the first formulation in the next generation of equations of state.

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Table 1

other properties \ given function	$h(s,p)$	$f(v,t)$	$p(v,T)$
p	p	$-\frac{\partial f}{\partial v}$	p
T	$\frac{\partial h}{\partial s}$	T	T
v	$\frac{\partial h}{\partial p}$	v	v
s	s	$-\frac{\partial f}{\partial T}$	$-\int_{v_o}^{v} \frac{\partial p}{\partial T}\, dv$
h	h	$f-T\frac{\partial f}{\partial T} - v\frac{\partial f}{\partial v}$	$-\int_{v_o}^{v} p\,dv - T\int_{v_o}^{v} \frac{\partial p}{\partial T}\, dv + pv$
c_p	$\frac{\frac{\partial h}{\partial s}}{\frac{\partial^2 h}{\partial s^2}}$	$-\frac{T\{\frac{\partial^2 f}{\partial v^2}\cdot\frac{\partial^2 f}{\partial T^2} - \frac{\partial^2 f}{\partial v \partial T}\}}{\frac{\partial^2 f}{\partial v^2}}$	$\frac{-T\{\frac{\partial p}{\partial v}\left[\int_{v_o}^{v} \frac{\partial^2 p}{\partial T^2}\, dv\right] + \left(\frac{\partial p}{\partial T}\right)^2\}}{\frac{\partial p}{\partial v}}$
f	$h-p\frac{\partial h}{\partial p} - s\frac{\partial h}{\partial s}$	f	$-\int_{v_o}^{v} p\, dv$

Table 2

b_{ij}

i \ j	0	1	2	3
0	$2.29396778966_{10}4$	$9.90221723853_{10}2$	$-9.22809517786_{10}1$	$3.44813660448_{10}0$
1	$1.49785098900_{10}4$	$7.05515999554_{10}2$	$-7.46436404816_{10}1$	$2.77856793062_{10}0$
2	$4.20456184702_{10}3$	$3.44974682900_{10}2$	$-3.93283089753_{10}1$	$1.44141411490_{10}0$
3	$6.47843041947_{10}2$	$9.93241195506_{10}1$	$-1.24112560347_{10}1$	$4.45137731177_{10}-1$
4	$4.47369162798_{10}1$	$1.36056524920_{10}1$	$-1.85857222935_{10}0$	$6.57125442419_{10}-2$

Table 3

Comparison of values derived from equation 10 with

1963 IST values and tolerances

COMPRESSED WATER

	Volume cm^3/g				Enthalpy J/g			
t^oC	0	50	100	150	0	50	100	150
p bar								
1(a)	1.00012	1.0121			0.059	209.38		
(b)	1.0002	1.0121			0.06	209.3		
(c)	-0.8	0			-0.1	0.8		
(d)	1	2			1	1		
5	0.9999	1.0119	1.0432	1.0905	0.465	209.7	419.4	632.0
	0.9999	1.0119	1.0433	1.0906	0.47	209.6	419.4	632.2
	0	0	-1	-1	-0.5	1	0	-2
	2	2	2	3	2	2	2	3
10	0.9996	1.0117	1.0430	1.0901	0.97	210.2	419.8	632.3
	0.9997	1.0117	1.0431	1.0903	0.98	210.1	419.7	632.4
	-1	0	-1	-2	-1	1	1	-1
	2	2	2	3	2	2	4	4
25	0.9989	1.0110	1.0422	1.0891	2.49	211.4	420.9	633.2
	0.9989	1.0110	1.0423	1.0894	2.50	211.3	421.0	633.4
	0	0	-1	-3	-1	1	-1	-2
	2	2	2	3	5	2	4	4
50	0.9976	1.0099	1.0410	1.0875	5.02	213.6	422.8	634.8
	0.9976	1.0099	1.0410	1.0878	5.05	213.5	422.8	634.9
	0	0	0	-3	-3	1	0	-1
	2	2	2	3	10	2	4	4
75	0.9964	1.0088	1.0397	1.0859	7.53	215.7	424.7	636.3
	0.9964	1.0088	1.0398	1.0862	7.58	215.7	424.7	636.5
	0	0	-1	-3	-5	0	0	-2
	2	2	3	4	15	2	4	4
100	0.9951	1.0077	1.0385	1.0842	10.0	217.9	426.6	637.9
	0.952	1.0077	1.0386	1.0846	10.1	217.9	426.6	638.1
	-1	0	4	-4	-1	0	0	-2
	2	2	4	4	2	2	4	4
125	0.9939	1.0067	1.0373	1.0826	12.5	220.0	428.4	639.5
	0.9940	1.0066	1.0373	1.0830	12.6	220.0	428.5	639.7
	-1	1	0	-4	-1	0	-1	-2
	2	2	4	4	3	2	4	4
150	0.9927	1.0056	1.0361	1.0811	15.0	222.2	430.3	641.1
	0.9928	1.0055	1.0361	1.0813	15.1	222.1	430.4	641.3
	-1	1	0	-2	-1	1	-1	-2
	2	2	4	4	3	2	4	4
175	0.9915	1.0045	1.0349	1.0795	17.5	224.3	432.2	642.7
	0.9915	1.0044	1.0348	1.0798	17.6	224.3	432.3	642.9
	0	1	1	-3	-1	0	-1	-2
	2	2	4	4	4	3	4	4

	Volume cm^3/g				Enthalpy J/g			
p bar \ t °C	0	50	100	150	0	50	100	150
200	0.9903	1.0035	1.0337	1.0780	20.0	226.5	434.1	644.2
	0.9904	1.0033	1.0336	1.0782	20.1	226.5	434.2	644.5
	-1	2	1	-2	-1	0	-1	-3
	2	2	4	4	4	3	4	4
225	0.9891	1.0024	1.0325	1.0764	22.4	228.6	436.0	645.8
	0.9892	1.0023	1.0324	1.0766	22.6	228.6	436.1	646.1
	-1	1	1	-2	-2	0	-1	-3
	2	2	4	4	5	3	4	4
250	0.9879	1.0014	1.0313	1.0749	24.9	230.7	437.9	647.5
	0.9880	1.0012	1.0313	1.0751	25.1	230.7	438.0	647.7
	-1	2	0	-2	-2	0	-1	-2
	2	2	4	4	5	3	4	4
275	0.9868	1.0004	1.0301	1.0734	27.3	232.9	439.8	649.1
	0.9868	1.0002	1.0301	1.0736	27.5	232.8	439.8	649.3
	0	2	0	-2	-2	1	-1	-2
	2	2	4	4	5	3	4	4
300	0.9856	0.9993	1.0290	1.0720	29.8	235.0	441.7	650.7
	0.9856	0.9992	1.0289	1.0721	30.0	235.0	441.8	650.9
	0	1	1	-1	-2	0	-1	-2
	2	2	4	4	5	3	4	4
350	0.9833	0.9973	1.0267	1.0690	34.6	239.3	445.5	653.9
	0.9834	0.9972	1.0267	1.0692	34.9	239.2	445.6	654.1
	-1	1	0	-2	-3	1	-1	-2
	2	2	4	4	6	3	4	4
400	0.9810	0.9953	1.0245	1.0662	39.4	243.5	449.3	657.2
	0.9811	0.9951	1.0244	1.0664	39.7	243.5	449.4	657.4
	-1	2	1	-2	-3	0	-1	-2
	2	2	4	4	7	3	4	4
450	0.9788	0.9933	1.0222	1.0634	44.2	247.8	453.1	660.5
	0.9788	0.9932	1.0222	1.0636	44.6	247.7	453.2	660.7
	0	1	0	-2	-4	1	-1	-2
	2	2	4	4	8	4	4	4
500	0.9766	0.9913	1.0201	1.0607	49.0	252.0	256.9	663.8
	0.9766	0.9912	1.0200	1.0609	49.3	252.0	457.0	664.0
	0	1	1	-2	-3	0	-1	-2
	2	3	4	5	8	4	4	4
550	0.9745	0.9894	1.0179	1.0580	53.7	256.2	460.7	667.2
	0.9745	0.9892	1.0178	1.0582	54.1	256.2	460.8	667.3
	0	2	1	-2	-4	0	-1	-1
	3	3	4	5	8	4	4	4
600	0.9723	0.9875	1.0158	1.0554	58.4	260.4	464.5	670.5
	0.9723	0.9873	1.0157	1.0556	58.8	260.4	464.6	670.6
	0	2	1	-2	-4	0	-1	-1
	3	3	4	5	9	4	4	4
650	0.9703	0.9856	1.0138	1.0528	63.1	264.6	468.3	673.9
	0.9703	0.9854	1.0137	1.0530	63.5	264.6	468.4	674.0
	0	2	1	-2	-4	0	-1	-1
	3	3	4	5	10	4	4	5

Table 3 continued.....

$t^{o}C$	Volume cm^3/g				Enthalpy J/g			
p bar	0	50	100	150	0	50	100	150
700	0.9682	0.9838	1.0117	1.0503	67.7	268.8	472.1	677.3
	0.9682	0.9836	1.0116	1.0505	68.1	268.8	472.1	677.3
	0	2	1	-2	-4	0	0	0
750	0.9662	0.9820	1.0097	1.0479	72.4	273.0	476.0	680.7
	0.9662	0.9818	1.0096	1.0480	72.7	273.0	476.0	680.7
	0	2	1	-1	-3	0	0	0
	3	3	4	5	11	6	5	5
800	0.9642	0.9802	1.0078	1.0455	77.0	277.2	479.8	684.1
	0.9642	0.9800	1.0076	1.0456	77.3	277.1	470.8	684.0
	0	2	2	-1	-3	1	0	1
	3	3	4	5	12	7	7	7
850	0.9622	0.9784	1.0058	1.0432	81.5	281.4	483.6	687.5
	0.9622	0.9782	1.0057	0.0432	81.9	281.3	483.6	687.4
	0	2	1	0	-4	1	0	1
	3	3	4	5	12	8	8	8
900	0.9603	0.9767	1.0039	1.0409	86.1	285.5	487.4	690.9
	0.9603	0.9765	1.0038	1.0409	86.5	285.4	487.3	690.8
	0	2	1	0	-4	1	1	1
	3	3	4	5	12	9	9	9
950	0.9584	0.9750	1.0021	1.0387	90.6	289.7	491.2	694.4
	0.9584	0.9748	1.0019	1.0386	91.1	289.6	491.2	694.2
	0	2	2	1	-5	1	0	2
	3	3	4	5	12	10	10	10
1000	0.9566	0.9733	1.0002	1.0365	95.1	293.9	495.1	697.8
	0.9566	0.9731	1.0000	1.0363	95.7	293.7	495.0	697.6
	0	2	2	2	-6	2	1	2
	3	3	4	5	12	12	12	12

(a) equation (9) value

(b) IST value

(c) equation value - IST value

(d) IST tolerance

Table 4

Comparison of saturated liquid values with

1963 IST and its tolerances

$t^{o}C$	p bar	v_f cm^3/g eqn(10)	v_f cm^3/g IST	Δv	Tol.	h_f J/g eqn(10)	h_f J/g IST	Δh	Tol.
0	0.006108	1.00013	1.00021	-8	5	-0.0415	-0.0416	1	4
.01	0.006112	1.00013	1.00021	-8	5	0.000611	0.000611	0	1
10	0.012271	1.00032	1.0004	-0.8	1	42.00	41.99	1	4
20	0.023368	1.0018	1.0018	0	1	83.91	83.86	5	8
30	0.042418	1.0044	1.0044	0	1	125.74	125.66	8	8
40	0.073750	1.0079	1.0079	0	1	167.52	167.47	5	8
50	0.12335	1.0121	1.0121	0	2	209.3	209.3	0	1
60	0.19919	1.0171	1.0171	0	2	251.1	251.1	0	1
70	0.31161	1.0227	1.0228	-1	2	293.0	293.0	0	1
80	0.47358	1.0290	1.0290	0	3	334.9	334.9	0	2
90	0.70109	1.0359	1.0359	0	3	377.0	376.9	1	2
100	1.01325	1.0434	1.0435	-1	3	419.1	419.1	0	2
110	1.4327	1.0515	1.0515	0	4	461.4	461.3	1	2
120	1.9854	1.0603	1.0603	0	4	503.8	503.7	1	2
130	2.7011	1.0697	1.0697	0	4	546.4	546.3	1	3
140	3.6136	1.0797	1.0798	-1	4	589.1	589.1	0	3
150	4.7597	1.0905	1.0906	-1	4	632.0	632.2	-2	3

Table 5

Comparison of saturated liquid values

t °C	p bar	v_f cm^3/g (9)	v_f cm^3/g eqn(10)	h_f J/g (9)	h_f J/g eqn(10)	s_f J/g K (9)	s_f J/g K eqn(10)	c_{p_f} J/g K eqn(11)	c_{p_f} J/g K eqn(10)
0	0.006107	1.00018	1.00013	-0.0416	-0.0415	-0.0002	-0.0001	4.218	4.214
.01	0.006111	1.00018	1.00013	0.00631	0.000611	0.0000	0.0000	4.218	4.214
10	0.012277	1.00039	1.00032	42.00	42.00	0.1510	0.1511	4.193	4.197
20	0.023378	1.0018	1.0018	83.86	83.91	0.2963	0.2965	4.182	4.186
30	0.042433	1.0044	1.0044	125.66	125.74	0.4365	0.4368	4.179	4.180
40	0.073774	1.0078	1.0078	167.45	167.52	0.5721	0.5724	4.179	4.177
50	0.123383	1.0121	1.0121	209.25	209.30	0.7035	0.7037	4.181	4.179
60	0.19924	1.0171	1.0171	251.08	251.11	0.8310	0.8311	4.184	4.183
70	0.31166	1.0227	1.0227	292.96	292.98	0.9548	0.9549	4.190	4.189
80	0.47364	1.0290	1.0290	334.90	334.92	1.0753	1.0753	4.196	4.197
90	0.70112	1.0360	1.0359	376.93	376.96	1.1925	1.1926	4.205	4.207
100	1.01325	1.0435	1.0434	419.05	419.11	1.3069	1.3070	4.216	4.218
110	1.4326	1.0516	1.0515	461.30	461.38	1.4185	1.4187	4.229	4.231
120	1.9853	1.0603	1.0603	503.7	503.8	1.528	1.528	4.245	4.244
130	2.7011	1.0697	1.0697	546.3	546.4	1.634	1.635	4.263	4.259
140	3.6135	1.0798	1.0797	589.1	589.1	1.739	1.739	4.285	4.274
150	4.7597	1.0905	1.0905	632.1	632.0	1.842	1.841	4.310	4.289

TABLE 8

$t^{\circ}C$	p bar	dp	.0005 p	h J/g	dh	s J/g K	ds
			Boundary between Regions I and II				
1000	2806.3	.002645	1.40	4127.9	.000615	5.9285	.000000
800	2011.1	.002645	1.01	3501.2	.000615	5.5444	"
600	1174.5	.002645	.59	2789.1	.000615	5.0223	"
500	743.7	.002645	.37	2432.4	.000717	4.7099	
450	530.1	.002645	.27	2248.2	.000715	4.5299	"
400	323.7	.002594	.16	2051.3	.000697	4.3164	"
380	245.4	-.001440	.12	1966.9	-.000247	4.2166	"
375	226.7	.000809	.11	1946.4	.000272	4.1917	"
374	223.1	.002633	.11	1938.5	.000612	4.1810	"
373	219.6	.004004	.11	1933.4	.000931	4.1744	"
372	216.2	.002627	.11	1928.0	.000611	4.1673	"
371.5	214.5	-.000563	.11	1925.2	-.000131	4.1636	"
371.3	213.8	-.002612	.11	1924.0	-.000607	4.1620	"
			Boundary between Regions II and III				
1000	9097.6	-.005620	4.5	4267.2	-.001108	5.2501	.000000
800	6837.5	-.006650	3.4	3470.7	-.001275	4.8136	"
600	4473.6	-.008117	2.2	2647.6	-.001510	4.2728	"
500	3234.6	-.009096	1.6	2221.4	-.001663	3.9450	"
400	1947.8	-.0010289	.97	1782.3	-.001842	3.5623	"
300	621.6	.117417	.31	1323.7	.014313	3.0942	"
280	356.4	.117487	.18	1229.5	.014326	2.9865	"
260	94.1	.117195	.047	1134.2	.014298	2.8722	"
258	68.0	.117167	.034	1124.6	.014295	2.8604	"
256	42.1	.117138	.021	1115.0	.014293	2.8485	"
			Boundary between Regions III and IV				
1000	21433.5	.003366	10.7	5006.5	.000723	4.7837	.000000
800	17465.0	.003388	8.7	4095.6	.000752	4.3360	"
600	13334.1	.003374	6.7	3160.3	.000787	3.7765	"
400	9095.2	.003124	4.6	2187.7	.000815	3.0356	"
200	4698.4	.000904	2.3	1153.9	.000637	1.9485	"
0	1118.5	-.041505	.56	105.6	-.003885	-0.0125	-.000001

Appendix 1

Summary of equations and coefficients

(1) Vapour pressure of saturated water

$$\ln\beta = \sum_{i=0}^{11}{}' A_i T_i(q)$$

where $q = \{2(\frac{1}{\theta} - 0.95)^{0.4} - A_{12}\}/A_{13}$

$\theta = \frac{T}{T_{cl}}$ and $\beta = \frac{p}{p_{cl}}$

A_0	= -8.119 364 2	A_7	= $1.245\ 539\ 9\times10^{-4}$
A_1	= 5.132 255 5	A_8	= $-4.915\ 428\ 8\times10^{-5}$
A_2	= -1.184 240 7	A_9	= $4.630\ 256\ 5\times10^{-5}$
A_3	= $1.177\ 959\ 2\times10^{-1}$	A_{10}	= $1.530\ 133\ 4\times10^{-5}$
A_4	= $-5.157\ 642\ 0\times10^{-3}$	A_{11}	= $-2.095\ 453\ 0\times10^{-5}$
A_5	= $-1.468\ 953\ 7\times10^{-3}$	A_{12}	= 1.452 207 17
A_6	= $5.362\ 281\ 8\times10^{-4}$	A_{13}	= -0.848 789 53

(2) Specific volume of saturated liquid

$$\frac{1}{\chi} = \sum_{i=0}^{10}{}' B_i T_i(r)$$

where $r = 1 - 2(1 - \frac{t}{t_{cl}})^{0.4}$

and $\chi = \frac{v}{v_{cl}}$

B_0	= 4.332 053	B_6	= $-3.765\ 370\times10^{-3}$
B_1	= -1.107 796	B_7	= $1.123\ 345\times10^{-3}$
B_2	= $-5.275\ 102\times10^{-2}$	B_8	= $-2.458\ 266\times10^{-3}$
B_3	= $2.173\ 547\times10^{-2}$	B_9	= $-1.425\ 530\times10^{-3}$
B_4	= $-1.754\ 636\times10^{-2}$	B_{10}	= $-1.304\ 721\times10^{-3}$
B_5	= $5.125\ 009\times10^{-3}$		

(3) Saturated liquid α equation

$$\frac{\alpha}{p_{cl}\, v_{cl}} = \sum_{i=0}^{11}{}' C_i T_i(w)$$

where $w = (2(\frac{1}{\theta} - 0.99)^{0.5} - C_{12})/C_{13}$

C_0	= 2.262 821	C_7	= $8.949\ 914\times10^{-5}$
C_1	= 1.164 542	C_8	= $-2.309\ 905\times10^{-5}$
C_2	= $-1.529\ 470\times10^{-2}$	C_9	= $1.352\ 658\times10^{-5}$
C_3	= $-6.087\ 624\times10^{-2}$	C_{10}	= $-5.909\ 329\times10^{-6}$
C_4	= $-1.233\ 320\times10^{-2}$	C_{11}	= $-2.335\ 760\times10^{-6}$
C_5	= $6.246\ 461\times10^{-4}$	C_{12}	= 1.274 631 9
C_6	= $6.365\ 584\times10^{-4}$	C_{13}	= -1.074 631 9

(4) The saturation properties h_f and s_f are evaluated from the following equations:

$$h_f = \alpha + T\, v_f \frac{dp}{dT}$$

$$[s_f]_{T_t}^{T} = [h_f]_{T_t}^{T} + \int_{T_t}^{T} \frac{\alpha}{T^2}\, dT$$

(5) Atmospheric volume equation

$$v_A = \sum_{i=0}^{9} D_i T_i(Q)$$

where $Q = {}^{t}/75 - 1$

D_0	= 1.035 337 8	D_5	= $-5.758\ 072\ 5\times10^{-5}$
D_1	= $4.586\ 415\ 9\times10^{-2}$	D_6	= $1.809\ 699\ 1\times10^{-5}$
D_2	= $9.803\ 300\ 8\times10^{-3}$	D_7	= $-4.850\ 423\ 9\times10^{-6}$
D_3	= $-5.132\ 654\ 1\times10^{-4}$	D_8	= $2.381\ 440\ 1\times10^{-6}$
D_4	= $2.855\ 835\ 5\times10^{-4}$	D_9	= $-1.566\ 218\ 6\times10^{-6}$

(6) v-p-t compressed water equation

$$\frac{v}{v_A} = 1 + \sum_{i=0}^{5} \sum_{j=1}^{3} d_{ij}\, t^i (p - p_A)^j \quad \text{___(10)}$$

$d_{01} = -5.09769 \times 10^{-5}$ $\quad d_{02} = 8.2627 \times 10^{-9}$ $\quad d_{03} = -9.109 \times 10^{-13}$

$d_{11} = 3.71999 \times 10^{-7}$ $\quad d_{12} = -1.3794 \times 10^{-10}$ $\quad d_{13} = 2.626 \times 10^{-14}$

$d_{21} = -7.01760 \times 10^{-9}$ $\quad d_{22} = 3.4032 \times 10^{-12}$ $\quad d_{23} = -8.913 \times 10^{-16}$

$d_{31} = 6.00227 \times 10^{-11}$ $\quad d_{32} = -3.6432 \times 10^{-14}$ $\quad d_{33} = 1.1467 \times 10^{-17}$

$d_{41} = -3.09041 \times 10^{-13}$ $\quad d_{42} = 2.0836 \times 10^{-16}$ $\quad d_{43} = -7.102 \times 10^{-20}$

$d_{51} = 5.93416 \times 10^{-16}$ $\quad d_{52} = -4.1744 \times 10^{-19}$ $\quad d_{53} = 1.4841 \times 10^{-22}$

(7) h-p-s compressed water equation

$$h = \sum_{i=0}^{4}{}' \sum_{j=0}^{3}{}' b_{ij}\, T_i(x)\, T_j(y) \quad \text{___(9)}$$

The coefficients b_{ij} are given in Table 2

where $x = (2s - 11.99)/12.01$

and $y = (2p - 1000)/1000$

Defined constant quantities

$T_t = 273.16\ ^{o}K$

$T_{cl} = 647.3\ ^{o}K$

$P_{cl} = 221.2$ bar

$v_{cl} = 3.17\ cm^3/g$

All the equations to which reference is made in the text are reproduced in this appendix for the convenience of the reader so that he is not required to refer to the original papers.

The derivation of the saturation equations in sections (1), (2), (3) and (4) below is described by the authors (9), section (5) gives the equation for v_A published already (12), section (6) repeats the equation of Kell and Whalley (11) and section (7) gives the h-p-s equation of this paper.

APPENDIX 2

Chebyshev polynomial

The function $T_r(x)$ is the Chebyshev polynomial (or T-polynomial) of rth degree with x normalised in the range $-1 \leq x \leq 1$. The first two T-polynomials are $T_o(x) = 1$ and $T_1(x) = x$.

The remaining T-polynomials are calculated using the recurrence relation

$$T_n(x) = 2xT_{n-1}(x) - T_{n-2}(x).$$

Hence $T_2(x) = 2x^2 - 1$; $T_3(x) = 4x^3 - 3x$; etc.

In a Chebyshev series of the form

$$y = \sum_{r=0}^{n}{}' a_r T_r(x) \qquad (i)$$

the a_r are the Chebyshev coefficients, and the prime indicates that the first term of the sum is to be halved. Hence (i) can be written

$$y = \tfrac{1}{2}a_o + a_1 T_1(x) + a_2 T_2(x) + \ldots . a_n T_n(x).$$

Summation

There is a simple method for the summation of a Chebyshev series, which has the advantage of keeping round-off errors to a minimum.

The values $b_n, b_{n-1}, b_{n-2}, \ldots\ldots, b_0$ are formed successively from

$$b_r = 2x\, b_{r+1} - b_{r+2} + a_r \ , \quad b_{n+1} = b_{n+2} = 0$$

Then

$$y = \tfrac{1}{2}(b_0 - b_2)$$

Derivatives

On differentiating y with respect to x in equation (i) we obtain

$$\frac{dy}{dx} = \sum_{r=0}^{n-1}{}' A_r T_r(x)$$

where $A_{r-1} = A_{r+1} + 2ra_r$

and $A_n = A_{n+1} = 0$

A description of Chebyshev polynomials is given in Chapter 8 of Modern Computing Methods, 2nd edition (N.P.L. Notes on Applied Science, No.16, H.M.S.O., 1961).

Appendix 3

Properties of Compressed Water for Thermodynamic Testing of Turbines and Pumps

Prepared by K. S. Leong

Average isentropic coefficient of pressure enthalpy, A'_s, for water taking the lower pressure to be atmospheric

Pressure, atm.	Temperature, °C											
	0	2	4	5	10	14	15	16	20	30	40	50
0.9	1.00013	1.00003	1.00000	1.00001	1.00027	1.00073	1.00087	1.00103	1.00177	1.00434	1.00782	1.01208
1.1	1.00013	1.00003	1.00000	1.00000	1.00027	1.00072	1.00087	1.00103	1.00177	1.00434	1.00781	1.01208
25.0	0.99951	0.99942	0.99940	0.99941	0.99969	1.00016	1.00030	1.00046	1.00121	1.00379	1.00727	1.01154
50.0	0.99887	0.99879	0.99877	0.99879	0.99909	0.99957	0.99972	0.99988	1.00063	1.00323	1.00671	1.01098
75.0	0.99824	0.99816	0.99815	0.99817	0.99849	0.99898	0.99913	0.99929	1.00006	1.00267	1.00615	1.01042
100.0	0.99760	0.99754	0.99754	0.99756	0.99789	0.99839	0.99855	0.99871	0.99948	1.00211	1.00560	1.00986
125.0	0.99697	0.99692	0.99692	0.99695	0.99730	0.99781	0.99797	0.99813	0.99891	1.00155	1.00505	1.00931
150.0	0.99635	0.99630	0.99631	0.99634	0.99671	0.99723	0.99739	0.99756	0.99835	1.00099	1.00450	1.00875
175.0	0.99572	0.99568	0.99571	0.99574	0.99612	0.99665	0.99681	0.99699	0.99778	1.00044	1.00395	1.00821
200.0	0.99510	0.99507	0.99510	0.99514	0.99554	0.99608	0.99624	0.99642	0.99722	0.99989	1.00341	1.00766

$$A'_s = \frac{A_s}{v_o} = \frac{1}{v_o(P_1 - P_2)} \int_2^1 \left(\frac{\partial h}{\partial p}\right)_s dp$$

$$\left(\frac{\partial h}{\partial p}\right)_s = v$$

$$v_o = 1 \text{ cm}^3/\text{g} \text{ or } \frac{1}{62.4263} \text{ ft}^3/\text{lb}$$

$$1 \text{ atm.} = 1.03323 \text{ kp/cm}^2 = 14.6959 \text{ lbf/in}^2$$

Average isothermal coefficient of pressure enthalpy, A'_T, for water taking the lower pressure to be atmospheric

Pressure, atm.	Temperature, °C											
	0	2	4	5	10	14	15	16	20	30	40	50
0.9	1.01888	1.00911	0.99994	0.99556	0.97534	0.96083	0.95739	0.95402	0.94112	0.91207	0.88616	0.86229
1.1	1.01886	1.00910	0.99993	0.99555	0.97533	0.96082	0.95738	0.95401	0.94111	0.91206	0.88615	0.86228
25.0	1.01701	1.00735	0.99827	0.99393	0.97392	0.95956	0.95615	0.95281	0.94004	0.91127	0.88557	0.85188
50.0	1.01510	1.00553	0.99655	0.99225	0.97245	0.95824	0.95488	0.95157	0.93893	0.91044	0.88497	0.86147
75.0	1.01320	1.00373	0.99484	0.99059	0.97100	0.95694	0.95361	0.95034	0.93783	0.90962	0.88437	0.86105
100.0	1.01132	1.00195	0.99315	0.98894	0.96956	0.95565	0.95235	0.94912	0.93674	0.90880	0.88377	0.86063
125.0	1.00946	1.00018	0.99148	0.98731	0.96813	0.95437	0.95111	0.94791	0.93565	0.90798	0.88317	0.86021
150.0	1.00762	0.99844	0.98982	0.98570	0.96672	0.95310	0.94987	0.94670	0.93458	0.90717	0.88257	0.85979
175.0	1.00580	0.99671	0.98817	0.98410	0.96532	0.95184	0.94864	0.94551	0.93350	0.90636	0.88198	0.85937
200.0	1.00400	0.99499	0.98655	0.98251	0.96392	0.95059	0.94742	0.94432	0.93244	0.90556	0.88139	0.85895

$$A'_T = \frac{A_T}{v_o} = \frac{1}{v_o(P_1 - P_2)} \int_2^1 \left(\frac{\partial h}{\partial p}\right)_T dp$$

$$\left(\frac{\partial h}{\partial p}\right)_T = v - T\left(\frac{\partial v}{\partial T}\right)_P$$

$$v_o = 1 \text{ cm}^3/\text{g or } \frac{1}{62.4263} \text{ ft}^3/\text{lb}$$

$$1 \text{ atm.} = 1.03323 \text{ kgf/cm}^2 = 14.6959 \text{ lbf/in}^2$$

Average specific heat at constant pressure, c'_p, for water taking the lower temperature to be 15 °C

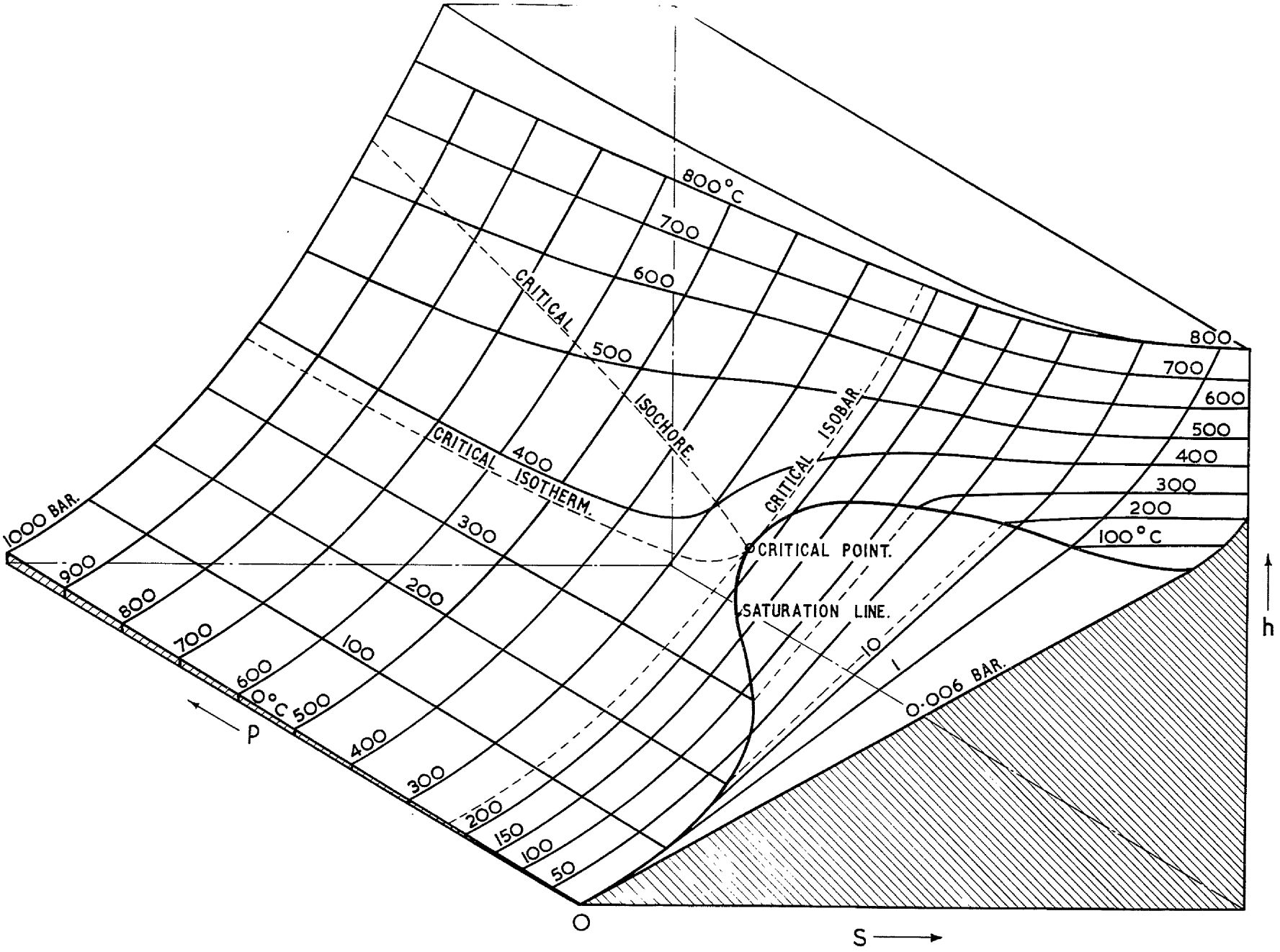
Pressure, atm.	Temperature, °C										
	0	2	4	5	10	14	16	20	30	40	50
0.9	1.0027	1.0021	1.0016	1.0013	1.0003	0.9998	0.9996	0.9992	0.9986	0.9983	0.9983
1.0	1.0026	1.0021	1.0015	1.0013	1.0003	0.9998	0.9996	0.9992	0.9986	0.9983	0.9983
1.1	1.0026	1.0021	1.0015	1.0013	1.0003	0.9998	0.9996	0.9992	0.9986	0.9983	0.9983
25.0	1.0003	0.9998	0.9993	0.9991	0.9982	0.9978	0.9976	0.9973	0.9968	0.9967	0.9967
50.0	0.9979	0.9974	0.9971	0.9969	0.9961	0.9958	0.9956	0.9954	0.9951	0.9950	0.9951
75.0	0.9955	0.9952	0.9948	0.9947	0.9941	0.9938	0.9937	0.9936	0.9933	0.9933	0.9935
100.0	0.9932	0.9929	0.9927	0.9925	0.9921	0.9919	0.9918	0.9917	0.9916	0.9917	0.9920
125.0	0.9910	0.9907	0.9905	0.9904	0.9901	0.9900	0.9900	0.9899	0.9899	0.9901	0.9905
150.0	0.9888	0.9886	0.9885	0.9884	0.9882	0.9882	0.9881	0.9882	0.9883	0.9886	0.9890
175.0	0.9866	0.9865	0.9864	0.9864	0.9863	0.9863	0.9864	0.9865	0.9867	0.9871	0.9875
200.0	0.9845	0.9844	0.9844	0.9844	0.9844	0.9846	0.9846	0.9848	0.9851	0.9856	0.9861

$$c'_p = \frac{c_p}{J} = \frac{1}{J(T_1 - T_2)} \int_2^1 \left(\frac{\partial h}{\partial T}\right)_p dT$$

$$\left(\frac{\partial h}{\partial T}\right)_p = c_p$$

J = 426.935 kgfm/Kcal = 1400.70 ft lbf/C.h.u.

1 atm. = 1.03323 kgf/cm^2 = 14.6959 lbf/in^2



h-p-s surface of water substance.

Fig. 1

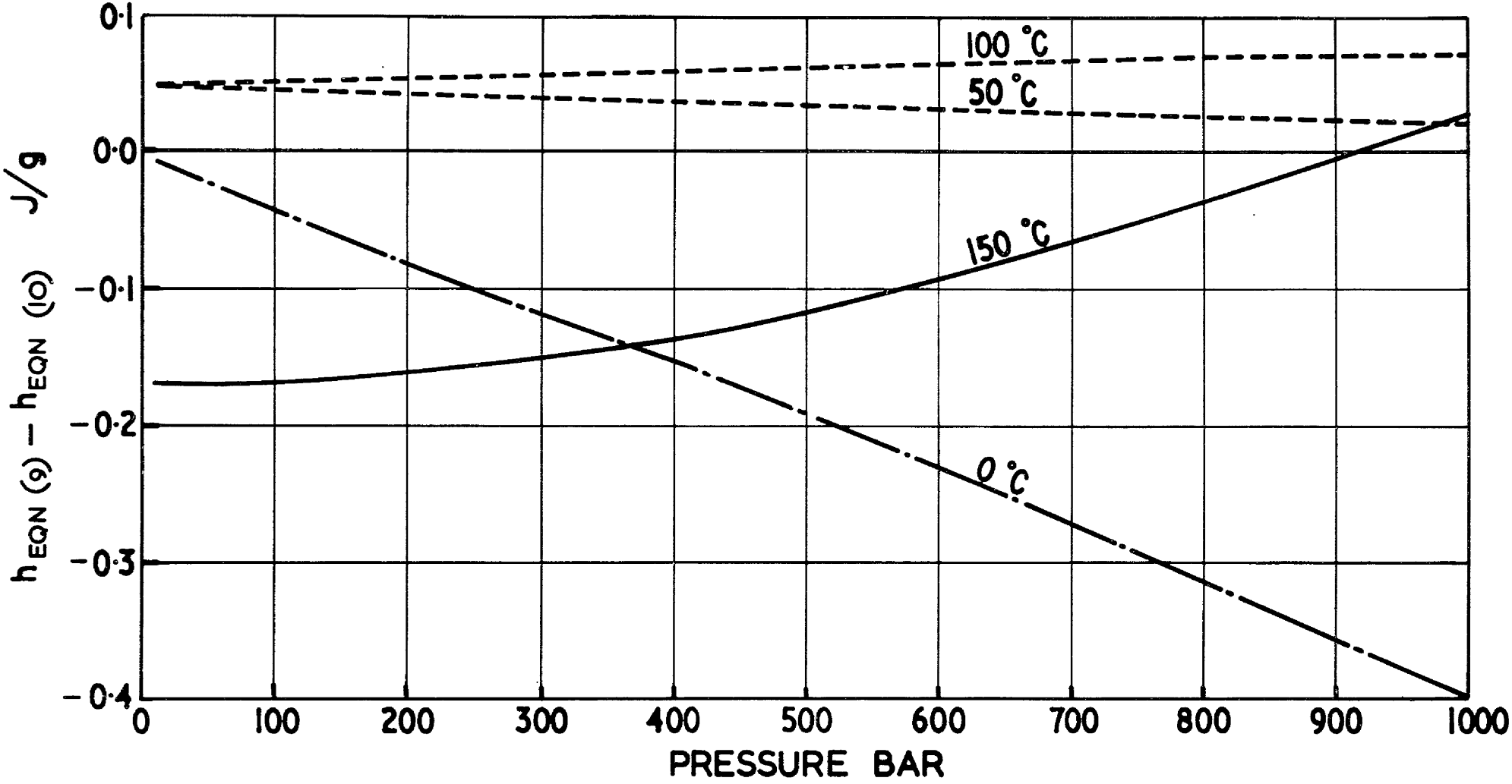

0·1
0·0
−0·1
−0·2
−0·3
−0·4
$h_{EQN}(9) - h_{EQN}(10)$ J/g
100 °C
50 °C
150 °C
0 °C
0
100
200
300
400
500
600
700
800
900
1000
PRESSURE BAR

Fig. 2.

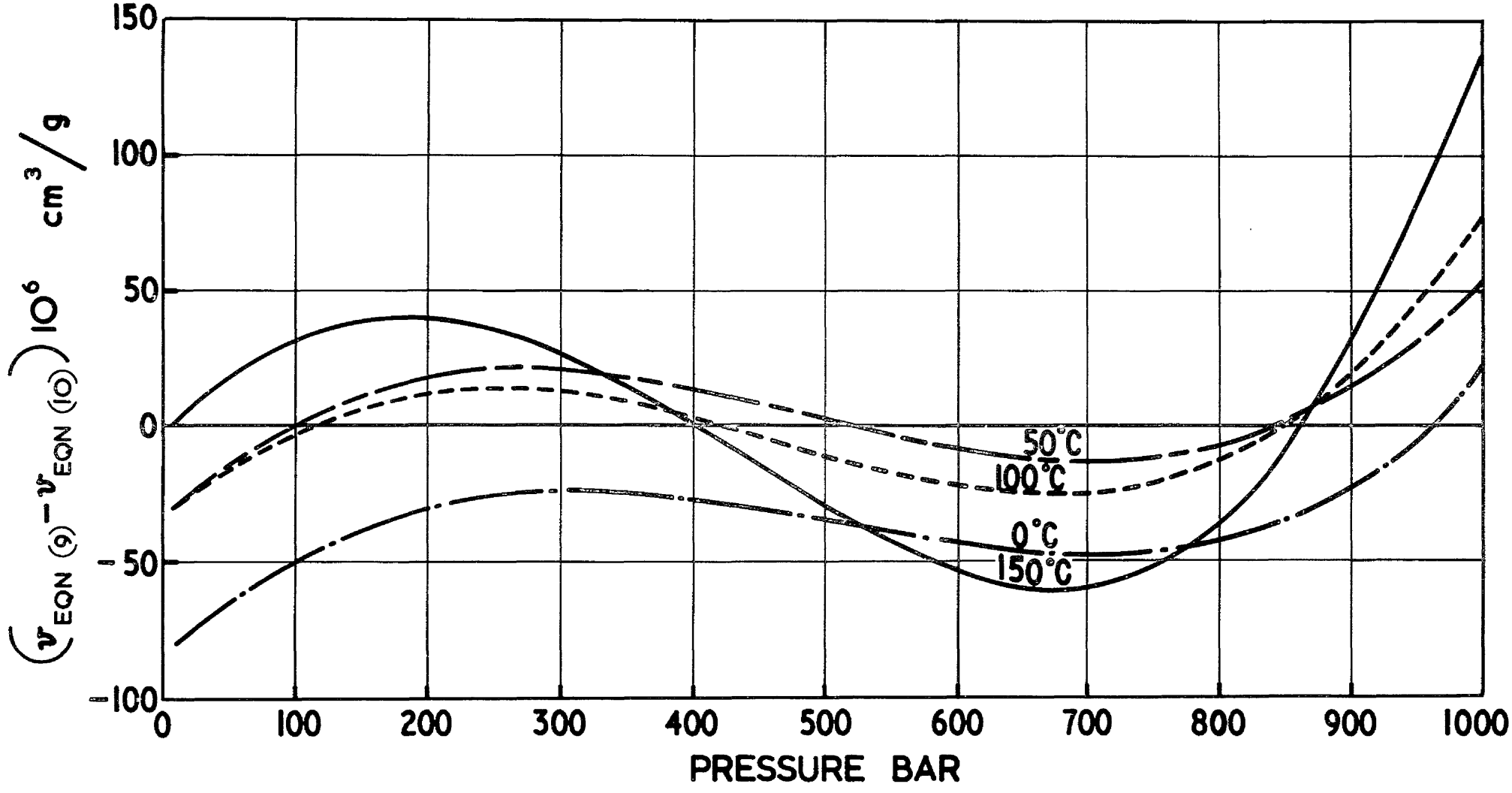

150
100
50
0
-50
-100
0
100
200
300
400
500
600
700
800
900
1000
PRESSURE BAR
$(v_{EQN\ (9)} - v_{EQN\ (10)})\ 10^6$ cm^3/g
50°C
100°C
0°C
150°C

Fig. 3.

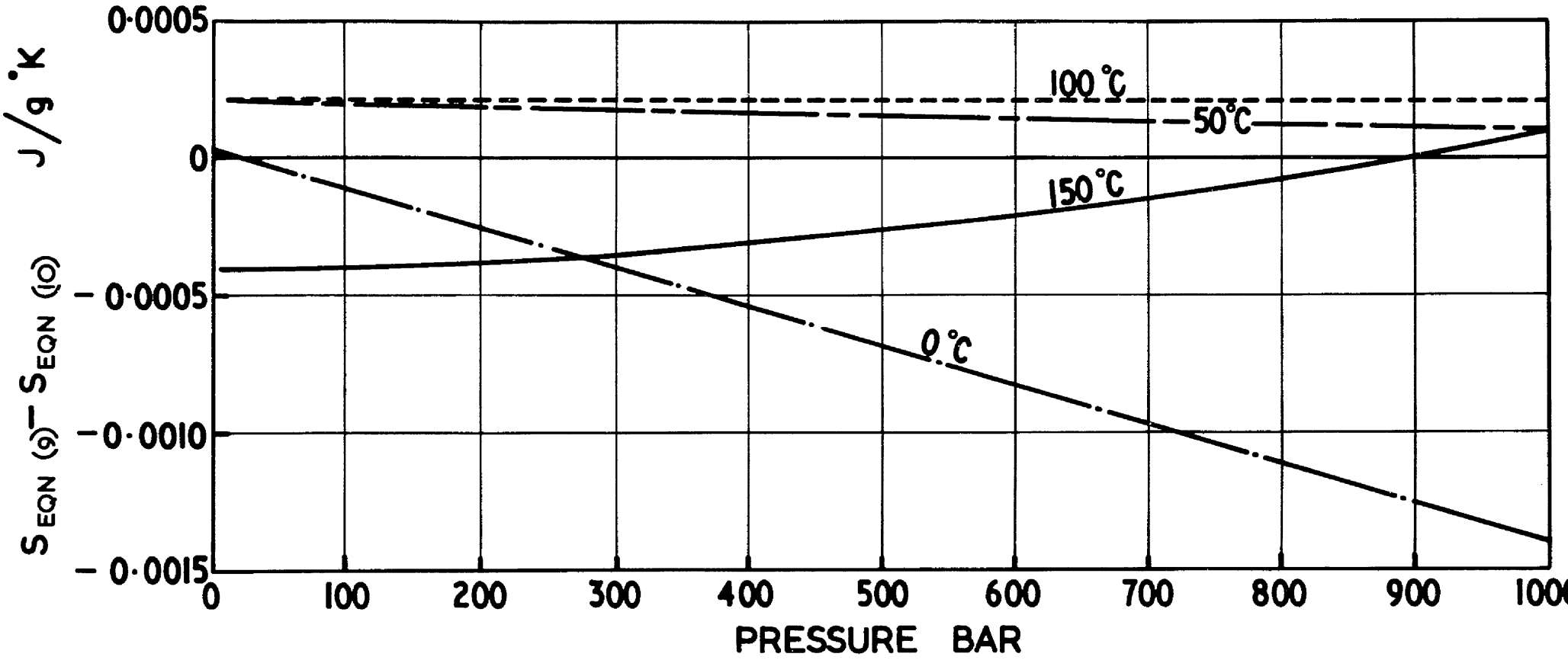

0·0005
0
−0·0005
−0·0010
−0·0015
$S_{EQN}(9) - S_{EQN}(10)$ J/g °K
100 °C
50°C
150 °C
0 °C
0
100
200
300
400
500
600
700
800
900
1000
PRESSURE BAR

Fig. 4.

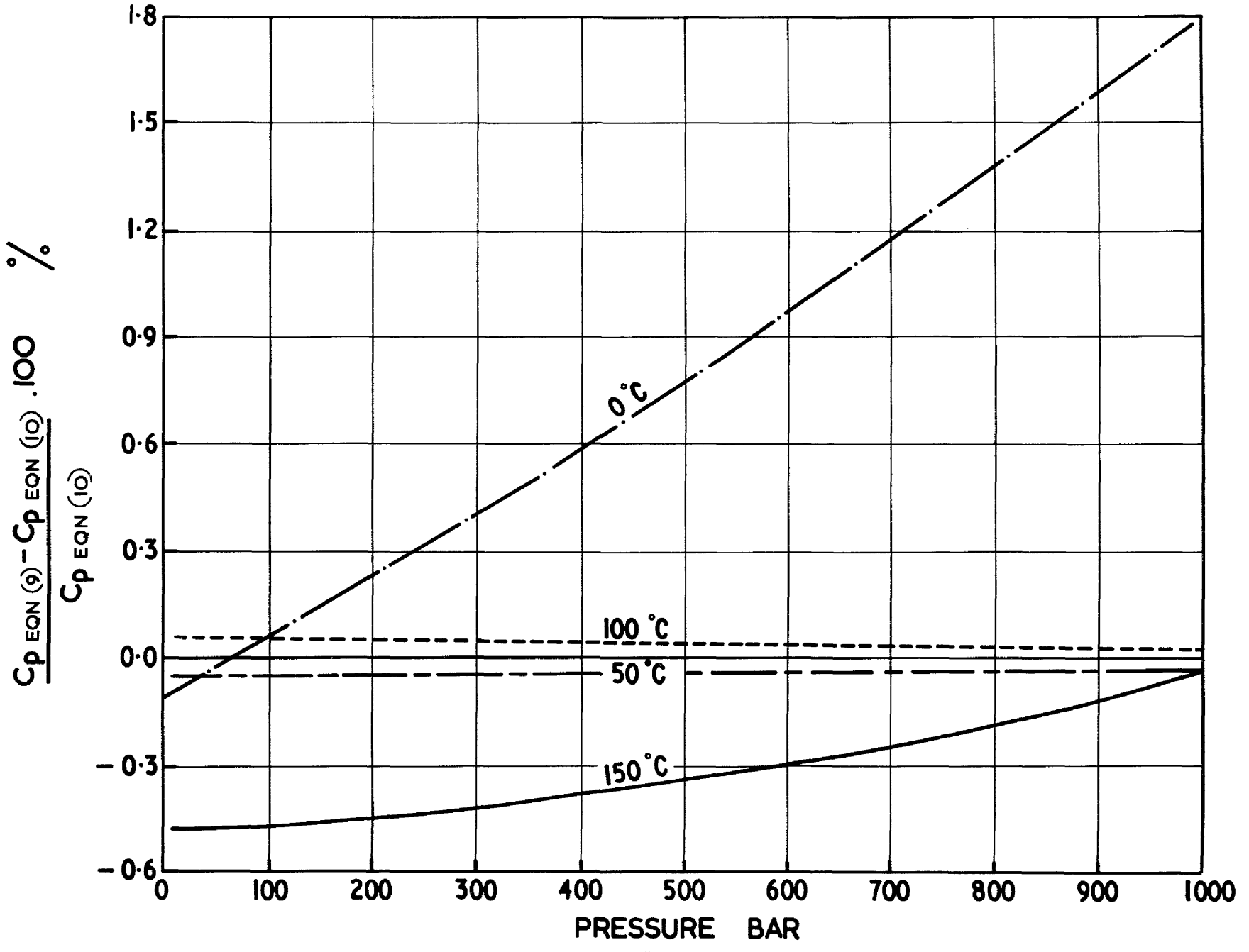

1·8
1·5
1·2
0·9
0·6
0·3
0·0
−0·3
−0·6
0
100
200
300
400
500
600
700
800
900
1000
0°C
100 °C
50 °C
150 °C
PRESSURE BAR
$\frac{C_{p\,EQN\,(9)} - C_{p\,EQN\,(10)}}{C_{p\,EQN\,(10)}} \cdot 100$ %

Fig. 5.

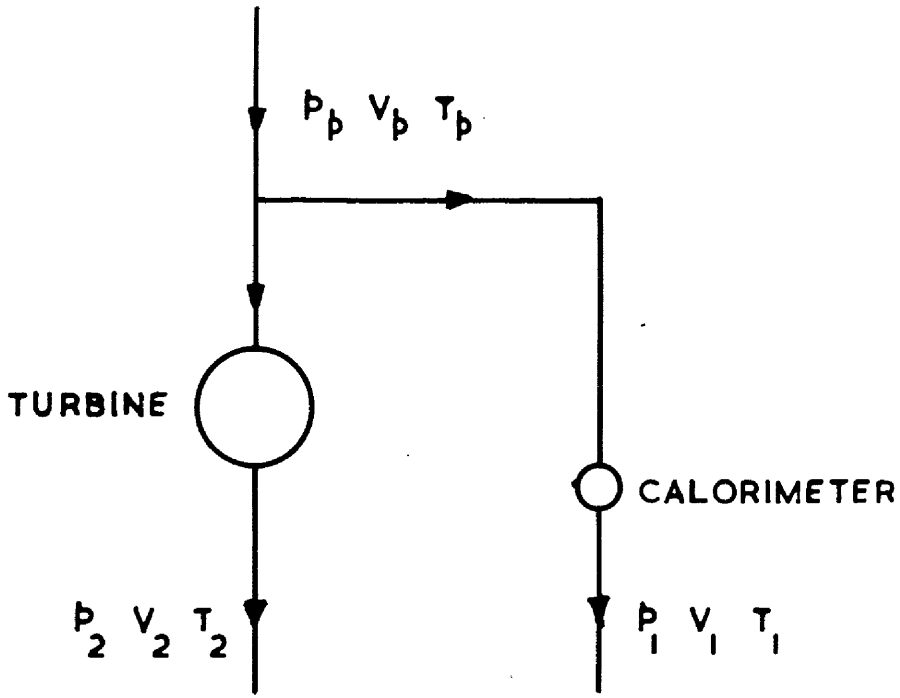


Fig 6

The Dynamic Viscosity of Compressed Water to 10 kilobar and Steam to 1500 °C

by

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Abstract

Equations specifying the dynamic viscosity of compressed water and steam are presented. In the temperature range 0 °C to 100 °C the location of the inversion locus ($\frac{\partial \eta}{\partial \rho_T} = 0$) is defined for the first time with some precision. The low pressure steam results are recorrelated and a higher inversion temperature is indicated than that previously accepted. From 100 °C to 600 °C values of viscosity are derived up to 3.5 kilobar and between 600 °C and 1500 °C up to 1 kilobar. All the original observations in the gaseous phase have been corrected to a consistent set of densities and deviation plots for all the new correlations are given.

Although the equations give values within the tolerances of the International Skeleton Tables it is clear that the range and tolerances of the latter could with some advantage be revised to give twice the existing temperature range and over ten times the existing pressure range at low temperatures. A list of the observations used and their deviations from the correlating equations is available as a separate publication.

Introduction

The first Skeleton Table (1) of the coefficient of viscosity of water and steam, covering ranges of pressure and temperature to 800 bar and 700 °C, were published by the Sixth International Conference on the Properties of Steam in November 1964. This table was drawn up on the basis of observations existing in 1962 and did not take account of work published later, in particular that of Latto (2) and Ray (3) at the University of Glasgow and that of Tanaka and associates (4) at the Resources Research Institute, Saitama, Japan. In view of this and as recently as 1966 the author (5) reviewed old and new sources of experimental work and by means of new correlating equations extended the upper limits of pressure and temperature to 1000 bar and 1000 °C. These new equations were marginally better than those appended to the Skeleton Table, if only, because the transition from the compressed water region (< 350 °C) to the supercritical steam region (> 375 °C)was improved.

The need to review yet again the current status of the viscosity of water and steam stems primarily from the observations of Bett and Cappi (6) and Horne and Johnson (7) on compressed water in the range 0 °C to 100 °C and the high pressure observations of Dudziak and Franck (8) in the range 160°C to 560 °C. These works enable the upper pressure to be raised to 10 kilobar in the range 0 °C to 100 °C and to 3.5 kilobar in the range 100 °C to 600 °C. At the same time it was decided to take the opportunity of revising all the older, and recognised, high pressure steam observations and relating them to one another through a consistent set of densities derived from the formulation of Juza (9). Account has also been taken of the measurements of Rivkin and Levin (10) in the low pressure region (< 300 °C) although the viscosity of superheated steam between 300 °C and 400 °C remains ill-defined due to the absence of experimental work.

1. Compressed water at sub-critical temperatures (< 375 °C)

The need to recorrelate the observations in the liquid phase stems from the recent work of Horne and Johnson (7), Dudziak and Franck (8) and Bett and Cappi (6), the latter contribution being especially important. Unfortunately,

these new observations are not of equivalent quality or quantity; in the temperature range being considered there are only 20 effective observations from the work of Dudziak and Franck and an uncertainty of about $\pm$ 5% has to be attached to each. The observations of Bett and Cappi cover the temperature range from 0 °C to 100 °C and up to 10 kilobar whereas the observations of Horne and Johnson cover only the temperature range from 0 °C to 20 °C and up to about 2 kilobar. Further, the observations of the former, made with a falling cylinder viscometer, exhibit a higher reproducibility than those of the latter, made with a rolling ball viscometer. A preliminary examination of these two sets of data in their common range from 0 °C to 20 °C shows that agreement is best at the upper and lower limits of temperature and that the greatest discrepancy occurs in the middle of the range.

The development of a new correlation for the liquid phase has to resolve a number of problems which may be summarised as follows:

(1) The new data, referred to above and discussed very briefly, is relative. In the works of Bett and Cappi and Horne and Johnson the experimental results are expressed in the form μ_p/μ_1 where μ_p is the viscosity at some pressure, p, and μ_1 is the viscosity at atmospheric pressure at the same temperature. Dudziak and Franck related their observations to the values at 800 bar in the International Skeleton Table, which does not now reflect the current state of knowledge.

A new equation for the one atmosphere - saturation line has to be devised since neither that appended to the IST nor that derived by Bruges (5) reflects the recognised values with sufficient precision. Any new equation must reflect the value of 1002×10^{-6} kg/m s for the dynamic viscosity of liquid water at one atmosphere pressure.

(2) The new data has to be merged with the older data which was reviewed by Bruges (5) and includes the following leading works, Swindells, Coe, and Godfrey (11), Schmidt and Mayinger (12), Moszynski (13), Tanaka (4) and Weber (14).

(3) Towards the critical point the values given by any new correlation have to coincide more or less with the correlations of Rivkin (15) which, in turn, agree very well with the IST values. Further, Rivkin estimates the value of viscosity at the critical point itself to lie between 40.2×10^{-6} and 41.8×10^{-6} kg/m s. Since equation 6, below, gives a value of 41.4×10^{-6} kg/m s at the critical point this was accepted as the end value for the saturated liquid line, thus relating the liquid values to the vapour values.

(4) The data of Bett and Cappi define very clearly the locus of the quantity $\frac{\partial \mu}{\partial \rho_T} = 0$. Previously, the inversion temperature, θ_o, was assumed to be independent of ρ, and, in fact, Weber estimated that viscosity was independent of pressure at 32 °C or 305 °K. The value was used by Kestin (16) in a correlation appended to the Skeleton Tables and later Bruges (5) used a value of 311 °K, in both instances the viscosity was expressed as a function of pressure and temperature. However, it is not possible to modify the previous approach and it is now essential to express the viscosity as a function of density and temperature, although the one atmosphere-saturation line remains as a function of temperature.

1.1 Correlation of Compressed Water at Sub-Critical Temperatures (< 375 °C)

All the data noted in the preceding section was used in a number of attempts to fit the data either by the method of 'least squares', or by the use of orthogonal Chebyshev polynomials, using procedures which previous experience had shown might be suitable. For this purpose an equation in the form of a Chebyshev series was devised to represent the viscosity values along the one atmosphere-saturation line, from 0 °C to 350 °C, which was to be used as a reference curve. However, due largely to the varying quality of the data and the need to apply the constraints referred to above it was decided to abandon this method of fitting. Instead it was decided to make a graphical representation of the data in terms of density and temperature, all the factors mentioned above being taken into account, and to fit the smoothed values so derived in place

of the actual observations themselves. The deviations of the actual experimental points from the final analytical expressions are shown in figures 1, 2 and 3.

The viscosity, μ at density ρ and temperature T, was expressed in the terms of the viscosity, μ_s, at one atmosphere or saturation density, ρ_s, at the same temperature by an equation of the form

$$\mu - \mu_s = \sum_{i=0}^{n} a_i (\rho - \rho_s)^n$$

A number of isotherms were so fitted using the graphed values of μ and ρ after which the coefficients 'a' were then fitted as functions of temperature to give $(\mu - \mu_s)$ as a double power series in T and $(\rho - \rho_s)$.

The one atmosphere- saturation line from 0 °C to 350 °C was replaced by two equations, one representing the viscosity of water at one atmosphere from 0 °C to 100 °C and a second representing the viscosity of the saturated liquid from 100 °C to 350 °C. Values of viscosity at one atmosphere pressure were generated at one degree intervals from 0 °C to 100 °C using the correlations of Bingham and White, Dorsey and others referred to by Bruges (5). The ratio μ/μ_{20} for equation 1† used here is compared with the older correlations in table 1.

Table 1

Values of μ_t/μ_{20} for water at one atmosphere pressure

t °C	Bingham & White (1912)	Hardy & Cottington (1949)	Weber (1955)	This work (eqn 1)
0	1.7864		1.7885	1.7824
5	1.5159	1.5154	1.5170	1.5110
10	1.2932		1.3043	1.3004
15	1.1312		1.1360	1.1347
20	1.0000	1.0000	1.0000	1.0000
25	0.8892		0.8885	0.8891
30	0.7948		0.7959	0.7968

continued over.....

†Equation numbers as used in appendix, where equations and their coefficients are listed.

t °C	Bingham & White (1912)	Hardy & Cottington (1949)	Weber (1955)	This work (eqn 1)
35	0.7184		0.7179	0.7189
40	0.6522	0.6518	0.6518	0.6526
50				0.5958
60		0.4656		0.4664
70				0.4039
80		0.3541		0.3546
90				0.3150
100		0.2816		0.2827

[Bingham, E.C. and White, G.F., Z. Phys. Chem. 80 (1912) 670

Hardy, R.C. and Cottington, R.L., Jl. Res. N.B.S., 48 (1949) 573

Weber, W., Z. Angew. Phys. 7 (2) (1955) 96]

Above 100 °C a series of "best" values were obtained at one degree intervals to 375 °C from the earlier work of Bruges and the latest correlation of Rivkin. The saturation values derived here from equation 2 are compared with those obtained previously in table 2.

Table 2

Values of viscosity of saturated liquid water

t °C	$\mu \times 10^6$ kg/m s Rivkin (15)	This work	IST
100	278.7	283.1	279.0
120	229.5	231.0	229.9
140	194.7	194.1	195.0
160	168.9	167.7	169.1
180	149.3	148.5	149.3
200	133.3	133.9	133.8
210	126.2	127.9	127.3
220	120.4	122.4	121.5
230	115.1	117.5	116.2
240	110.8	112.9	111.4
250	106.9	108.7	107.0

continued over.....

t	$\mu \times 10^6$ kg/m s		
°C	Rivkin (15)	This work	IST
260	103.2	104.8	103.0
270	99.8	101.1	99.4
280	96.4	97.5	96.1
290	93.2	94.1	93.0
300	89.9	90.7	90.1
310	86.5	87.2	-
320	83.0	83.5	-
330	79.0	79.5	-
340	74.8	74.8	-
350	70.0	69.4	-
360	64.4	62.1	-
370	56.4	51.8	-
374.15	$\{^{40.2}_{41.8}$	41.4	-

Because of their complexity none of the equations 1, 2, 3.1 and 3.2 for the liquid state is reproduced in the text and the reader is requested to refer to the appendix, where he is asked to note that the equations take the form of Chebyshev polynomials. The extent to which the equations represent the experimental observations may be judged by referring to the deviation plots of figures 1, 2 and 3.

Figure 1 (0 °C - 20 °C) shows the lack of agreement between the observations of Bett and Cappi and those of Horne and Johnson, except at 2 °C and 20 °C. The correlation favours the work of Bett and Cappi because of the wide range of pressure and temperature covered. However, older measurements of Timrot and Khlopkina (22) and Tanaka are adequately fitted by the equation.

Figure 2 (0 °C - 150 °C) includes the older measurements of Schmidt and Mayinger as well as those of Moszynski. At 75 °C the observations of Bett and Cappi could be low since there is good agreement at 50 °C and 100 °C. The data of Moszynski was estimated previously to be about 1% low and the new correlation bears this out.

Figure 3 (100 °C - 350 °C) shows the large scatter in the observations of Dudziak and Franck to which reference has already been made. The rest of the data is for the most part included within a band of ± 3%.

2. Steam at sub-critical pressures and temperatures

The viscosity of superheated steam, at temperatures between 100 °C and 300 °C, decreases with increasing density, a characteristic measured by Kestin and Wang (17) and earlier by Moszynski (18) using oscillating disc type viscometers. Later Kestin and Richardson (19), using the same type of instrument, refined the earlier observations and their simple correlating equation was used to generate the entries in the pertinent region of the 1964 International Skeleton Table. In 1966 the negative value of $\frac{\partial \mu}{\partial \rho}$ was confirmed by Rivkin and Levin, using a capillary viscometer, and the previous upper limit of temperature, 275 °C, achieved by Kestin and Richardson, was raised to 300 °C. Unfortunately, this temperature is still below that at which $\frac{\partial \mu}{\partial \rho} = 0$ or becomes positive, and the inversion temperature can only be found by extrapolation. A fairly good estimate of the inversion temperature can be obtained by plotting the actual experimental results to a convenient base, say pressure, and finding the value of viscosity, and hence the temperature, at which the viscosity is judged to be unvarying with pressure. The author carried this out and estimated the inversion temperature to be between 320 °C and 330 °C although the correlating equation of Kestin and Richardson indicates a value of 315 °C.

At the lower temperature (175 °C) the observations of Rivkin and Levin confirm those of Kestin and Richardson within 0.2% but along the 275 °C isotherm there is a systematic discrepancy reaching 2% between the two sets of results. Although the observations of the latter show a higher degree of reproducibility than those of the former the authors decided to include both sets in any correlation, being particularly anxious to derive all possible advantage from the 300 °C observations.

A number of attempts were made to correlate this low pressure data with the atmospheric pressure observations of Shifrin (20) and Latto over the temperature range 100 °C to 350 °C, giving various weighting factors to the low pressure data. None of the results was satisfactory since the purpose

was to provide simultaneously a good fit to the low pressure data and a consistent atmospheric line. Eventually the low pressure data, some 64 observations, were correlated using the same form of equation in density and temperature as that used by Kestin and Richardson. No advantage could be derived from a more elaborate equation and an improved correlating equation for this region can only be derived when additional observations above 300 °C become available.

2.1 Correlation for steam at sub-critical pressures and temperatures

The correlating equation, derived using the method of least squares, has the form

$$\mu = a + b\left(\frac{T}{T_o}\right) + c\left(\frac{T}{T_o}\right)^2 - \frac{\rho}{\rho_c}\left\{d + e\left(\frac{T}{T_o}\right)\right\} \qquad (4)$$

and may be considered valid in the ranges

$$0 \leq t \leq 326.93\ ^{\circ}C$$

$$0 \leq p \leq 165 \times 10^5\ N/m^2$$

A deviation plot for the assembly of observations is given in figure 4 from which it is readily seen that the equation represents a compromise between the two sets of data used. The temperature, at which the negative coefficient vanishes, is derived from the fourth term of equation 4 and is found to be 326.93 °C. Since there seemed no special merit in rounding this figure to 327 °C the authors retained the value of 326.93 °C.

3. Steam at atmospheric pressure

In view of the difficulty in fitting simultaneously the low pressure observations of Kestin and Richardson and Rivkin and Levin with the atmospheric measurements of Latto and Shifrin it was decided to accept the atmospheric values calculable from equation 4 in preference to those deduced from any correlation of the atmospheric observations. This means that the atmospheric line has to be constrained to give the values generated from equation 4 in the range 100 °C to 326.93 °C. Table 3 shows the intercomparison of four possible interpretations of the atmospheric line in the range 100 °C to 400 °C.

Table 3

Intercomparison of atmospheric equations in the range 100 °C - 400 °C

Dynamic viscosity, kg/m s x 10^6

°C	Latto (2)	Latto (2) & Shifrin (20)	L.P.data Eqn.4	Latto & Shifrin modified Eqn.5
100	12.14	12.154	12.064	12.072
110	12.54		12.474	12.476
120	12.94		12.884	12.882
130	13.34		13.295	13.288
140	13.75		13.705	13.697
150	14.15	14.150	14.117	14.106
160	14.56		14.528	14.516
170	14.97		14.940	14.928
180	15.38		15.352	15.341
190	15.79		15.765	15.754
200	16.21	16.182	16.178	16.169
210	16.62		16.591	16.584
220	17.04		17.005	17.000
230	17.45		17.419	17.417
240	17.87		17.834	17.834
250	18.29	18.241	18.249	18.252
260	18.71		18.664	18.670
270	19.13		19.080	19.089
280	19.55		19.497	19.508
290	19.97		19.914	19.927
300	20.39	20.319	20.331	20.347
310	20.81		20.749	20.767
320	21.23		21.167	21.187
330	21.66		21.586	21.607
340	22.08		22.005	22.027
350	22.50	22.408	22.424	22.447
360	22.92			22.866
370	23.34			23.286
380	23.77			23.705
390	24.19			24.124
400	24.61	24.500		24.543

The first column gives values of viscosity in micropoise derived from the publication of Latto and used by the author (5). The second column gives values, derived from a least squares fit to the fourth power in temperature of the data of Latto and Shifrin, and the third column gives the values derived from equation 4. Agreement between the entries in the three columns is remarkably close, better than 10^{-7} kg/m s except at the lower temperatures. It seemed likely that the atmospheric line could be represented over the range 0 °C to 1000 °C by an equation similar to that used to fit the data of Latto and Shifrin (column 2) but constrained to give the values of equation 4. The fourth column gives values derived from such an equation, which is not only a good fit at the lower temperatures but is also more than adequate at temperatures up to 1000 °C as can be seen from Table 4.

Table 4

Intercomparison of atmospheric equations, 500 °C-1000 °C

Dynamic viscosity, kg/m s x 10^6

°C	Latto (2)	Latto (2) & Shifrin (20)	Latto & Shifrin modified Eqn. 5
500	28.79	28.664	28.700
600	32.87	32.756	32.769
700	36.81	36.727	36.710
800	40.57	40.531	40.488
900	44.13	44.131	44.077
1000	47.50	47.492	47.459

3.1 Correlation for steam at atmospheric pressure

The correlating equation, derived as described in section 3, has the form

$$\mu = \sum_{i=0}^{4} f_i \left(\frac{T}{T_o}\right)^i \qquad (5)$$

and may be considered as valid in the range 100 °C to 1000 °C at atmospheric pressure (1.01325 x 10^5 N/m^2). Equation 5 gives the value of μ as 21.478 x 10^{-6} kg/m s at 326.93 °C as compared with 21.4570 x 10^{-6} kg/m s from equation 4.

No plot of deviations of experimental points from equation 5 is given since this would be virtually the same as those already published (2, 5).

4. Steam at supercritical temperatures (> 375 °C)

The leading works in this region are those of Timrot (21), Timrot and Khlopkina (22), Whitelaw (23), Ray (3), Schmidt and Mayinger (12) and Tanaka (4), to which list must be added the work of Dudziak and Franck (8). Apart from the latter reference all the other references have been discussed (5) and no further argument will be advanced here as to their quality as primary sources. The measurements of Dudziak and Franck are related to the values of viscosity quoted by various sources, including the author (24), at 800bar, and consequently are not primary determinations. Nevertheless, their observations provide the only guide, so far available, to the behaviour of the coefficient

of viscosity at pressures between 1000 x 10^5 N/m^2 and 3500 x 10^5 N/m^2 in the temperature range up to 500 °C. The scatter of their observations is such that an uncertainty of ± 5% has to be attached to their smoothed data.

In this region the "excess viscosity" is easily expressible as a function of density, the excess viscosity being equal to the difference between any measured value at a given pressure and temperature and the zero density value at the same temperature. In this case the zero density value was considered to be equivalent to the atmospheric value to a close approximation.

4.1 Correlation

The correlating equation has the form

$$\mu - \mu_1 = m(\frac{\rho}{\rho_c}) + n(\frac{\rho}{\rho_c})^2 \qquad \text{(6)},$$

where μ_1 is the atmospheric viscosity given by equation 5, and correlates all the data noted in section 4 with the exception of the observations of Dudziak and Franck. A deviation plot for the assembly of data used in the correlation is shown in figure 5.

Although it was decided to exclude the data of Dudziak and Franck, for the reasons given above, equation (6) is found to give values of viscosity which are nevertheless in good agreement with the smoothed data of Dudziak and Franck. Table 5 shows values of viscosity derived from equation 6 and the corresponding values from the aforementioned work.

Table 5

Viscosity values and ratios from Dudziak and Franck and equation 6

Dynamic viscosity, kg/m s x 10^6

p x 10^{-5} N/m^2	400 °C		500 °C		560 °C	
	D & F	Eqn.6	D & F	Eqn.6	D & F	Eqn.6
800	8.15	7.974	5.90	5.961	5.10	5.153
1000	8.75	8.444	6.65	6.742	5.85	5.922
2000	10.5	9.971	8.60	8.855	8.05	8.253
3000	11.6	10.98	9.65	10.09	9.15	9.592
3500	12.1	11.40	10.0	10.58	9.50	10.12
Ratios μ/μ_{800}						
800	1	1	1	1	1	1
1000	1.07	1.06	1.13	1.13	1.15	1.15
2000	1.29	1.25	1.46	1.49	1.58	1.60
3000	1.42	1.38	1.64	1.69	1.79	1.86
3500	1.48	1.43	1.69	1.77	1.86	1.96

It would seem that extrapolation of equation 6 to give viscosity values up to 3500 x 10^5 N/m^2 is justified within the temperature limits 375°C and 600°C. It is of interest to note that equation 6 involves terms in ρ and ρ^2 only, previously it had been thought necessary to include terms in ρ^3. In fitting the data so small a reduction in the standard deviation occurred, if a term in ρ^3 was included, that it was decided to omit the term in ρ^3.

Tables and Diagrams

The equations and their coefficients enable values of the dynamic viscosity of compressed water and steam to be calculated within the specified ranges of pressure and temperature. These ranges are shown in figure 5, together with upper limits of pressure and temperature of the Skeleton Tables, and those areas where graphical interpolation has still to be employed are identified. The equations give values which lie within the tolerances of the Skeleton Tables and table 6 sets out this comparison for a limited number of grid points. As might be expected the discrepancy between the IST values and those presented here is greatest for the liquid phase, particularly along the 0°C isotherm. The new correlation for the liquid phase shows that the temperature at which the negative density coefficient vanishes is 45°C, which is the same temperature at which the compressibility of the liquid is a minimum and is in accordance with the estimate of Horne and Johnson. Unfortunately the observations of these workers are not in very good agreement with the correlation except at 2°C and 20°C. However, some recent observations made by Wonham (25) using a rotating cylinder viscometer substantiate the work of Bett and Cappi and hence the correlation given here.

Values of dynamic viscosity at fairly wide intervals of pressure and temperature are given in tables 7 and 8 and a number of diagrams, figures 7 to 13, are presented which show the behaviour of this property over specific ranges of pressure and temperature. The magnitude of the density coefficient is particularly well displayed in figure 7 from which it may be seen that the negative coefficient vanishes about 45°C. Above this temperature the viscosity

of the liquid behaves normally and the isobars of the supercritical low temperature fluid merge smoothly with those of the high temperature fluid in the temperature range 250°C-375°C, particularly at pressures up to 1500 bar, as in figure 8. Steam at sub-critical pressures, like water at low temperatures, also exhibits a negative density coefficient and this is shown in figures 9 and 11. The blending of the isobars where the coefficient is negative ($< 326.93°C$) with the corresponding isobars at higher temperatures ($>375°C$) is troublesome due to the absence of experimental data. However by cross-plotting μ with p and t a reasonable merging is achieved as may be seen in figure 10. Figures 12 and 13 show the behaviour in the high temperature ranges up to 700°C and to 1500°C respectively.

Tables and diagrams at close intervals of temperature and pressure to permit easy interpolation have been prepared by the authors, from the equations presented here, for the Engineering Sciences Data Unit and these are available from the Institution as Engineering Sciences Data Item No. 68009.

Table 6

Comparison with IST values and tolerances

Dynamic Viscosity kg/m s x 10^6

p x 10^{-5} N/m^2 \ °C		0	100	200	300	400	500	600	700
1	(a)	1750	12.11	16.18	20.25	24.3	28.4	32.5	36.5
	(b)	1786	12.06	16.18	20.33	24.5	28.7	32.8	36.7
	(c)	40	0.12	0.16	0.20	0.7	0.8	1.0	1.1
200		1740	283	138	93.0	28.6	31.1	34.6	38.4
		1740	286	138	94.6	28.5	31.2	34.7	38.4
		40	7	4	2.3	1.1	1.2	1.4	1.5
400		1730	287	143	98.1	62.8	36.9	37.9	40.8
		1703	289	142	99.9	62.7	36.8	37.8	40.6
		70	12	6	3.9	2.5	1.5	1.5	1.6
600		1720	291	148	103.0	73.6	48.5	42.8	43.9
		1676	294	147	104.3	73.5	48.4	42.6	43.7
		70	12	6	4.0	2.9	1.9	1.7	1.8
800		1710	295	152	108.0	79.8	59.6	49.1	47.8
		1656	298	151	108.3	79.7	59.6	48.9	47.5
		70	12	6	4.0	3.2	2.4	2.0	1.9

(a) International Skeleton Table

(b) This work

(c) Tolerance

Table 7

Dynamic viscosity of water and steam, $\mu \times 10^6$ kg/m s

$p \times 10^{-5}$ N/m^2	°C 0	20	40	60	80	100	200	300	400	500	600	700	800	900	1000	1250	1500
1	1786	1002	653.9	467.3	355.3	12.06	16.18	20.33	24.54	28.70	32.77	36.71	40.49	44.08	47.46	54.95	61.15
200	1740	990.0	651.2	470.9	361.8	285.8	138.0	94.6	28.47	31.16	34.72	38.36	41.93	45.36	48.62	55.90	61.94
400	1703	983.8	651.6	475.6	368.7	289.4	142.4	99.9	62.73	36.76	37.83	40.64	43.78	46.94	50.00	56.96	62.81
600	1676	981.8	654.2	481.0	375.6	293.6	146.9	104.3	73.50	48.39	42.61	43.69	46.08	48.81	51.59	58.13	63.73
800	1656	982.9	658.4	486.7	382.2	298.2	151.2	108.3	79.74	59.61	48.93	47.50	48.81	50.96	53.38	59.40	64.70
1000	1644	986.1	663.7	492.7	388.4	303.0	155.5	112.1	84.44	67.42	55.60	51.83	51.90	53.36	55.35	60.76	65.71
1500	1638	1001	680.4	507.7	402.4	315.4	166.0	120.7	93.14								
2000	1661	1023	700.1	522.9	414.6	327.8	176.0	128.1	99.71								
2500	1706	1050	721.7	538.4	426.2	340.3	185.6	134.4	105.1								
3000	1765	1083	744.7	554.6	438.2	352.8	194.7	139.5	109.8								
3500	1836	1120	769.3	572.0	451.3	365.4	203.4	143.6	114.0								
4000	1916	1163	795.5	590.7	466.1	378.2											
5000	2092	1264	853.6	633.1	501.4	404.8											
6000	2282	1384	920.3	682.2	544.1	433.1											
7000	2476	1521	996.1	736.8	591.9	463.4											
8000	2668	1668	1081	795.2	641.4	495.7											
9000	2852	1818	1173	855.0	689.0	530.0											
10000	3021	1966	1271	913.7	730.5	565.9											

Table 8

Dynamic viscosity at saturation kg/m s

$t^{\circ}C$	$\mu_f \times 10^6$	$\mu_g \times 10^6$
0	1786	8.105
20	1002	8.903
40	653.9	9.701
60	467.3	10.50
80	355.4	11.29
100	283.1	12.06
120	231.0	12.83
140	194.1	13.57
160	167.7	14.30
180	148.5	15.02
200	133.9	15.72
220	122.4	16.42
240	112.9	17.14
260	104.8	17.90
280	97.5	18.74
300	90.7	19.73
320	83.5	20.95
340	74.8	22.70
360	62.1	26.5
370	51.8,	30.6
374.15	41.4	41.4

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List of Diagrams

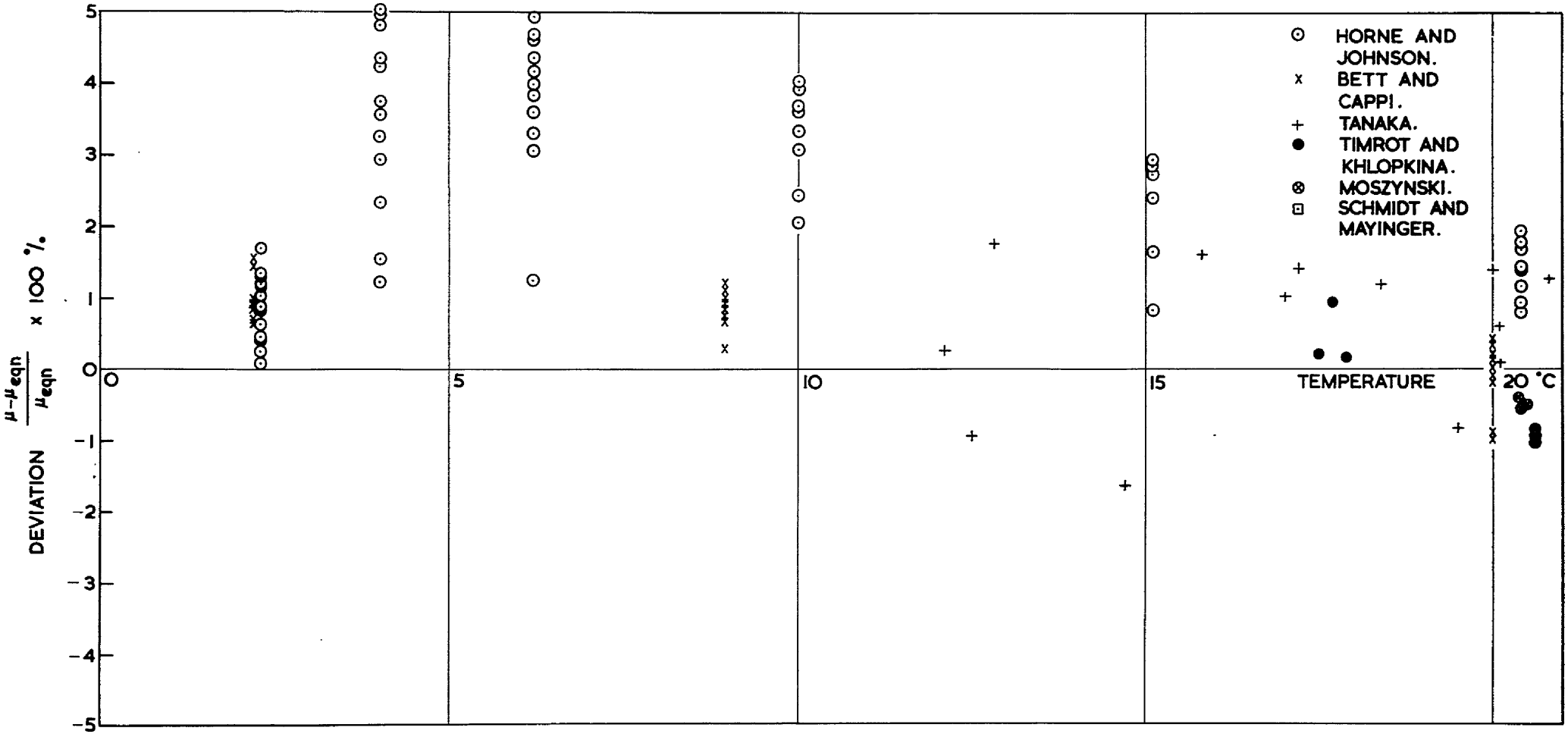

DEVIATION $\frac{\mu-\mu_{eqn}}{\mu_{eqn}}$ x 100 %
5
4
3
2
1
0
-1
-2
-3
-4
-5
0
5
10
15
20 °C
TEMPERATURE
HORNE AND JOHNSON.
BETT AND CAPPI.
TANAKA.
TIMROT AND KHLOPKINA.
MOSZYNSKI.
SCHMIDT AND MAYINGER.

Fig. 1

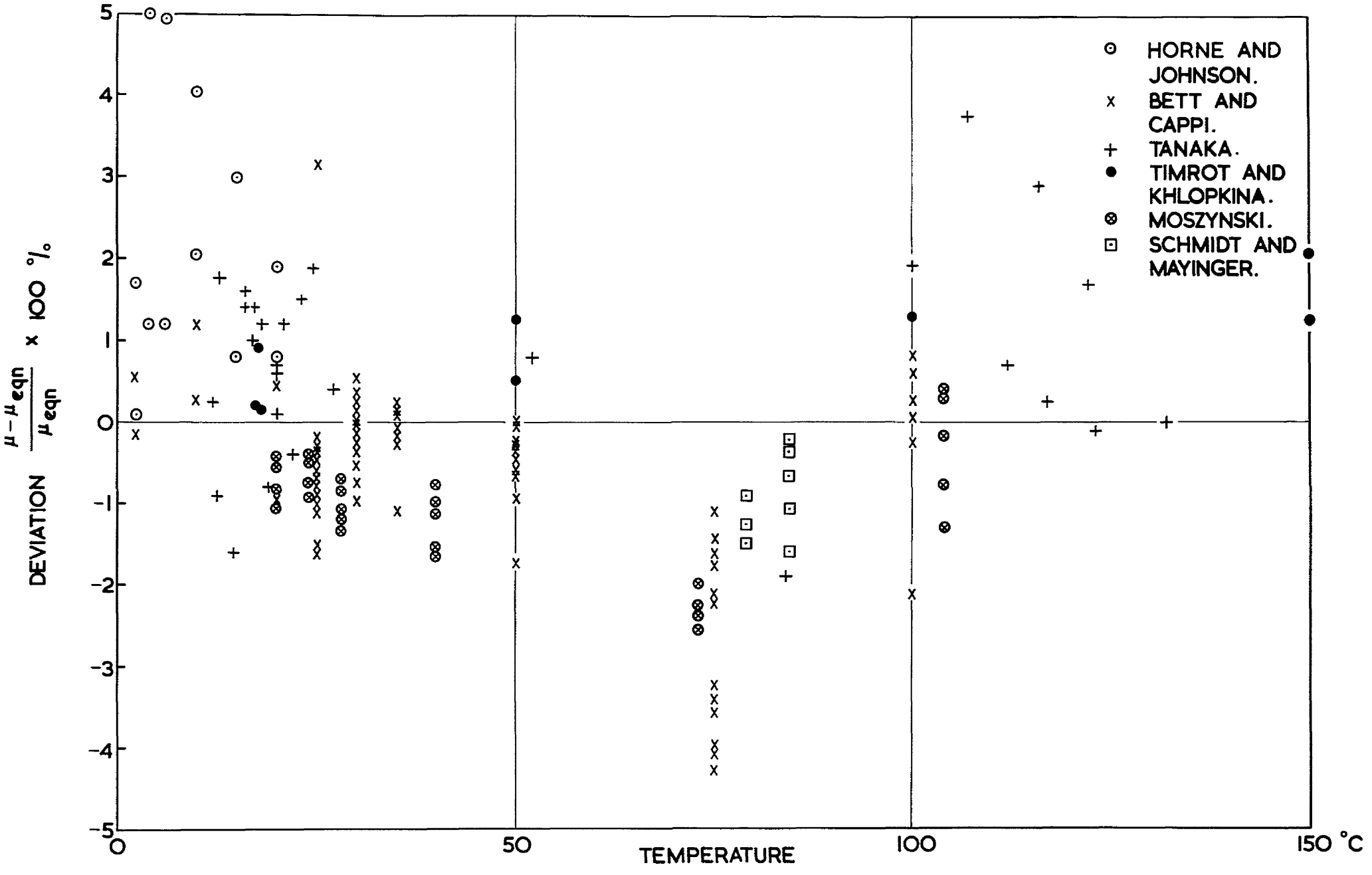

HORNE AND JOHNSON.
BETT AND CAPPI.
TANAKA.
TIMROT AND KHLOPKINA.
MOSZYNSKI.
SCHMIDT AND MAYINGER.
DEVIATION $\frac{\mu - \mu_{eqn}}{\mu_{eqn}} \times 100$ %
TEMPERATURE
5
4
3
2
1
0
-1
-2
-3
-4
-5
0
50
100
150 °C

Fig. 2

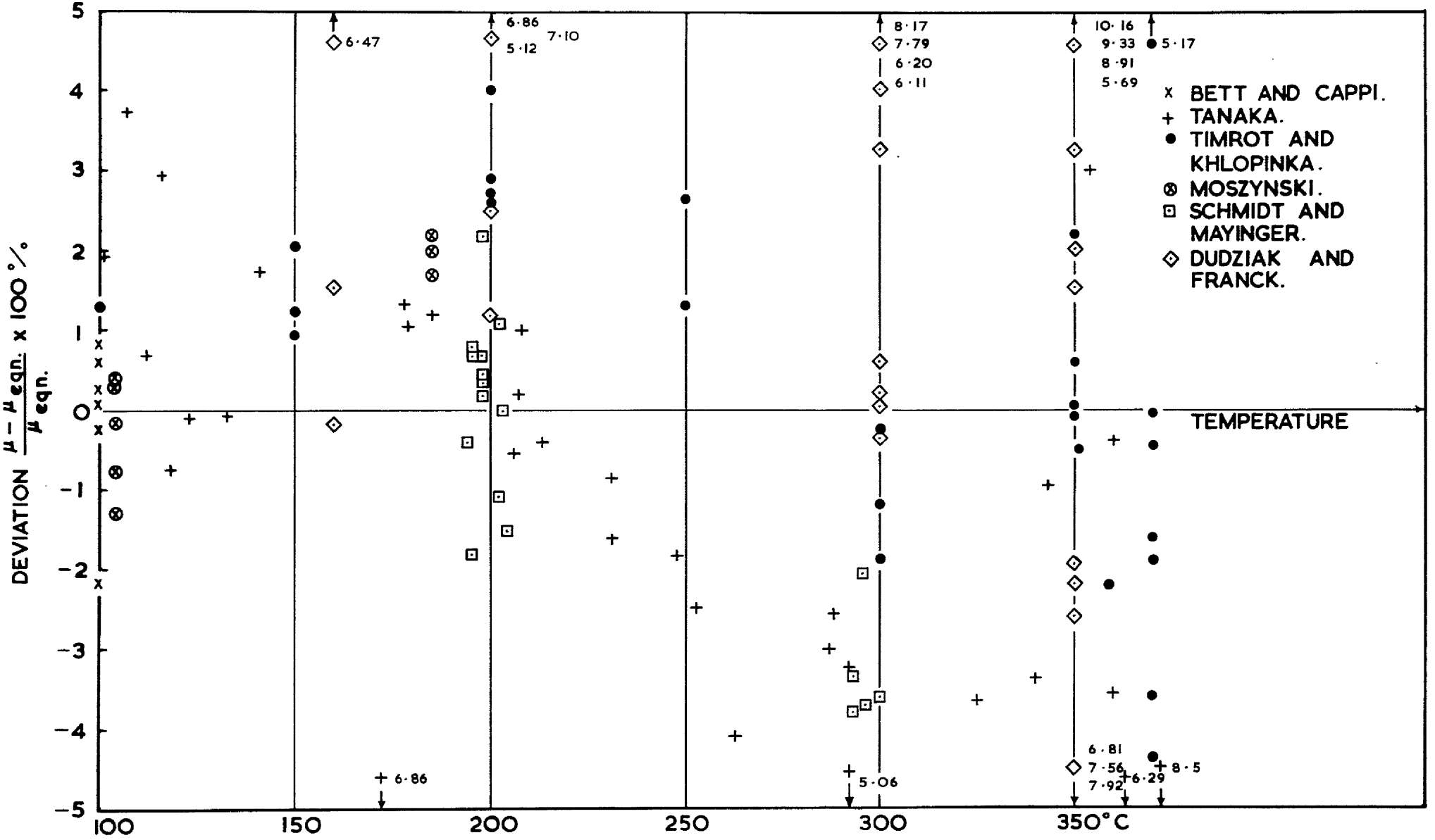

DEVIATION $\frac{\mu - \mu_{eqn.}}{\mu_{eqn.}} \times 100\,\%$
5
4
3
2
1
0
−1
−2
−3
−4
−5
100
150
200
250
300
350°C
TEMPERATURE
6·47
6·86
5·12
7·10
8·17
7·79
6·20
6·11
10·16
9·33
8·91
5·69
5·17
6·86
5·06
6·81
7·56
7·92
6·29
8·5
x BETT AND CAPPI.
+ TANAKA.
● TIMROT AND KHLOPINKA.
⊗ MOSZYNSKI.
⊡ SCHMIDT AND MAYINGER.
◇ DUDZIAK AND FRANCK.

Fig. 3

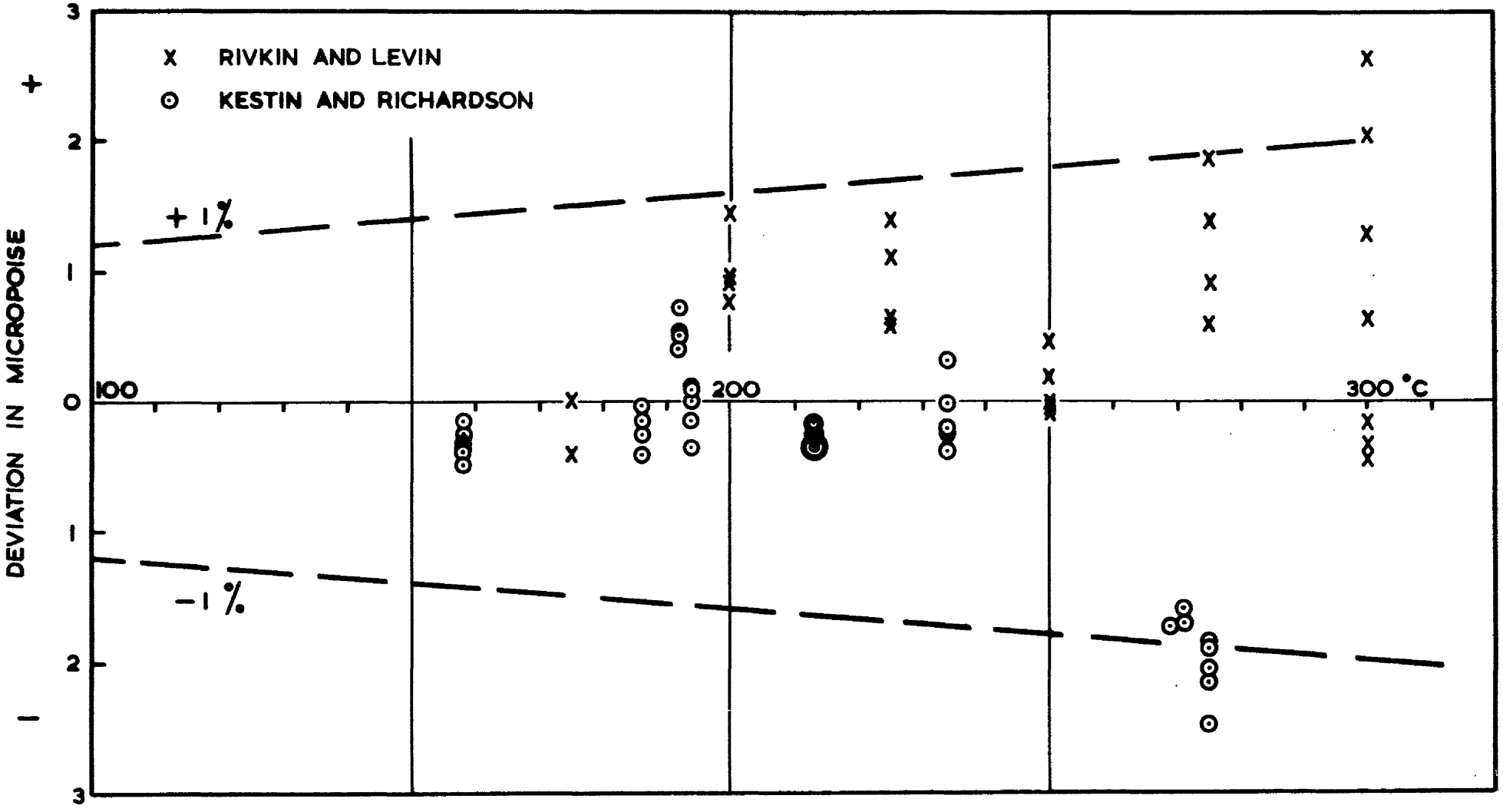
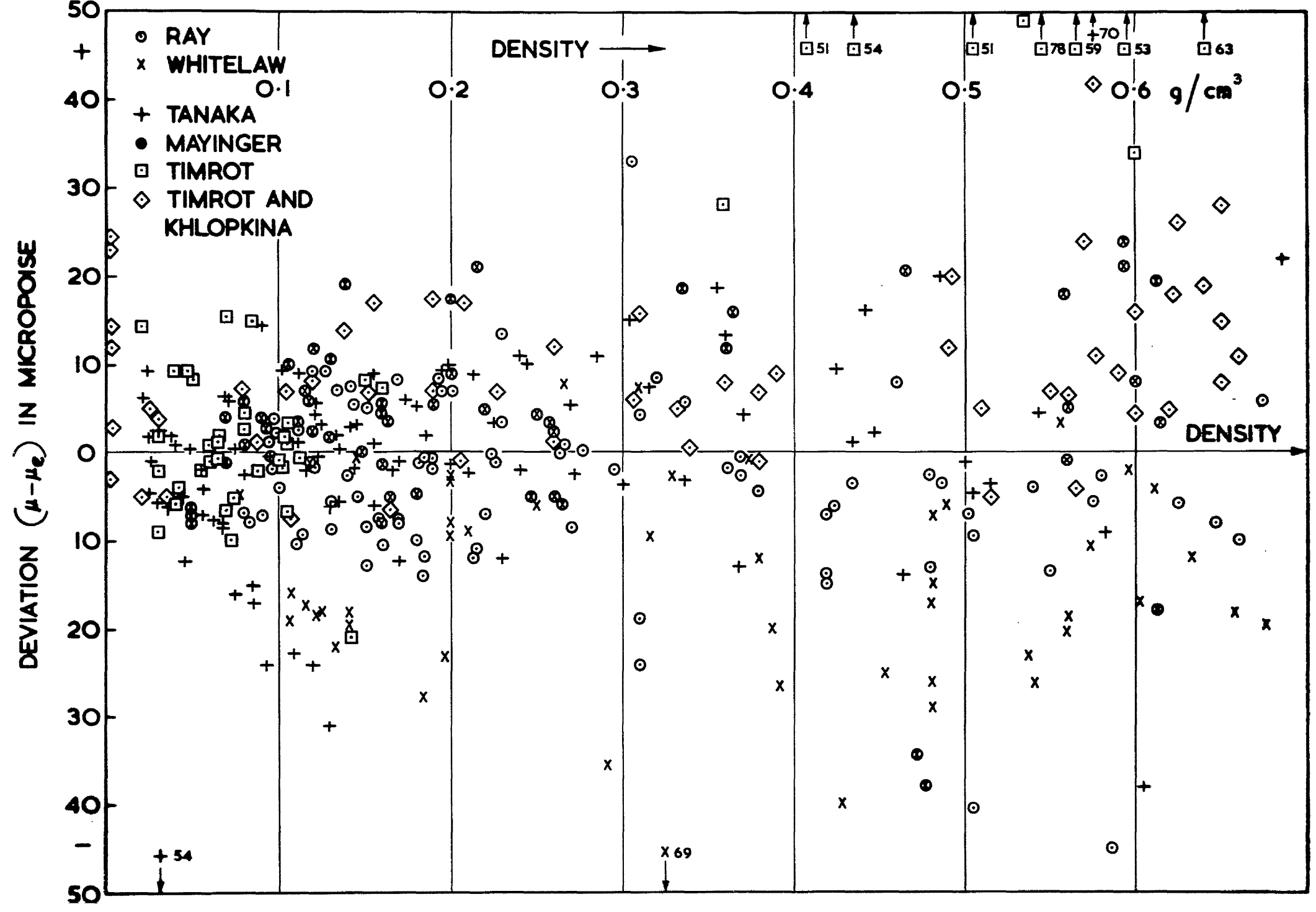

X RIVKIN AND LEVIN
⊙ KESTIN AND RICHARDSON
+ 1%
− 1%
100
200
300 °C
0
1
2
3
+
−
DEVIATION IN MICROPOISE

Fig. 4


RAY
WHITELAW
TANAKA
MAYINGER
TIMROT
TIMROT AND KHLOPKINA
DENSITY
0·1
0·2
0·3
0·4
0·5
0·6 g/cm³
51
54
51
78
59
+70
53
63
DENSITY
DEVIATION (μ−μe) IN MICROPOISE
50
40
30
20
10
0
10
20
30
40
50
+54
X69

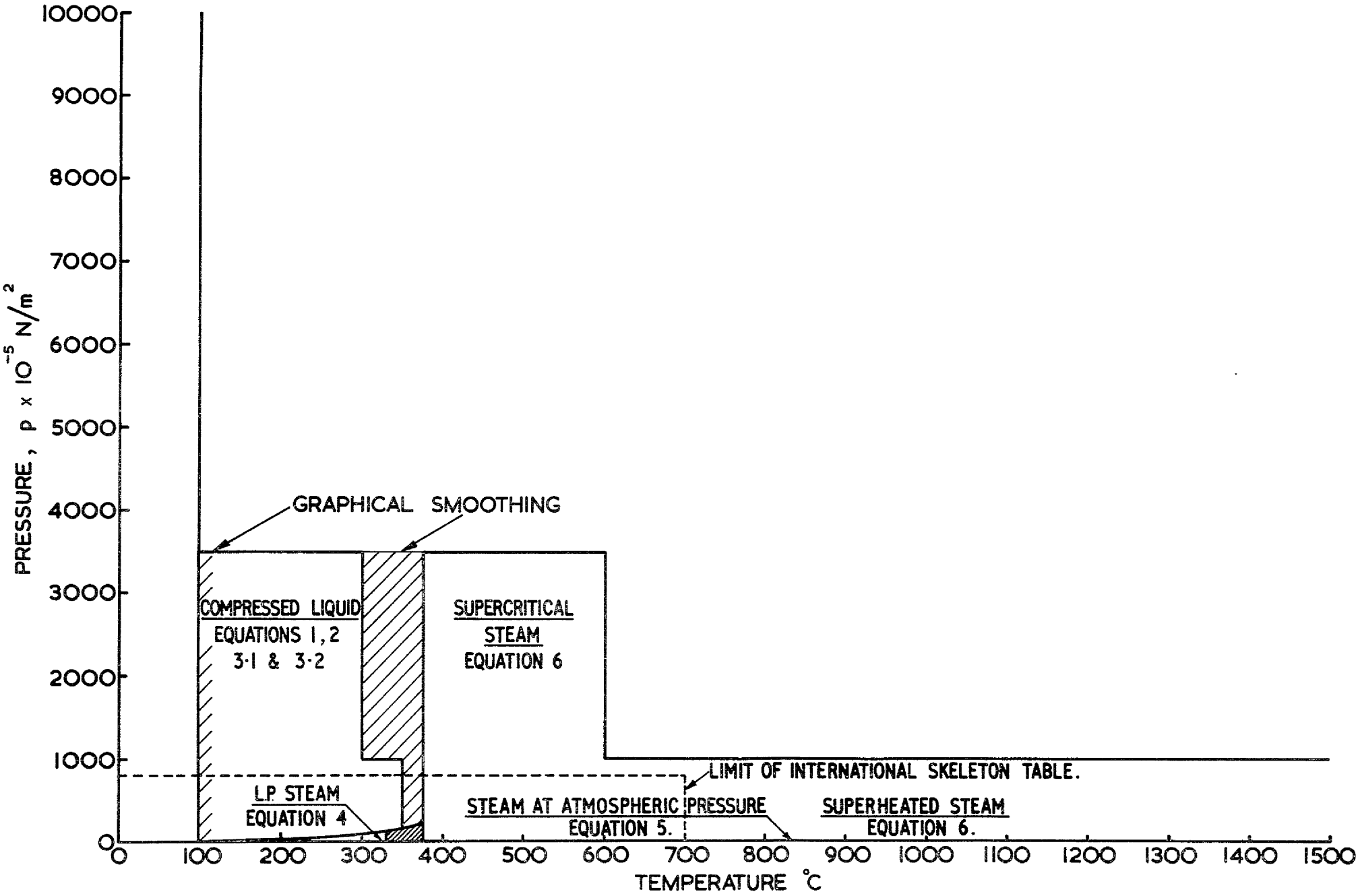

PRESSURE, p x 10^-5 N/m^2
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
GRAPHICAL SMOOTHING
COMPRESSED LIQUID
EQUATIONS 1, 2
3·1 & 3·2
SUPERCRITICAL
STEAM
EQUATION 6
LIMIT OF INTERNATIONAL SKELETON TABLE.
L.P. STEAM
EQUATION 4
STEAM AT ATMOSPHERIC PRESSURE
EQUATION 5.
SUPERHEATED STEAM
EQUATION 6.
0
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
1500
TEMPERATURE °C

Fig. 6

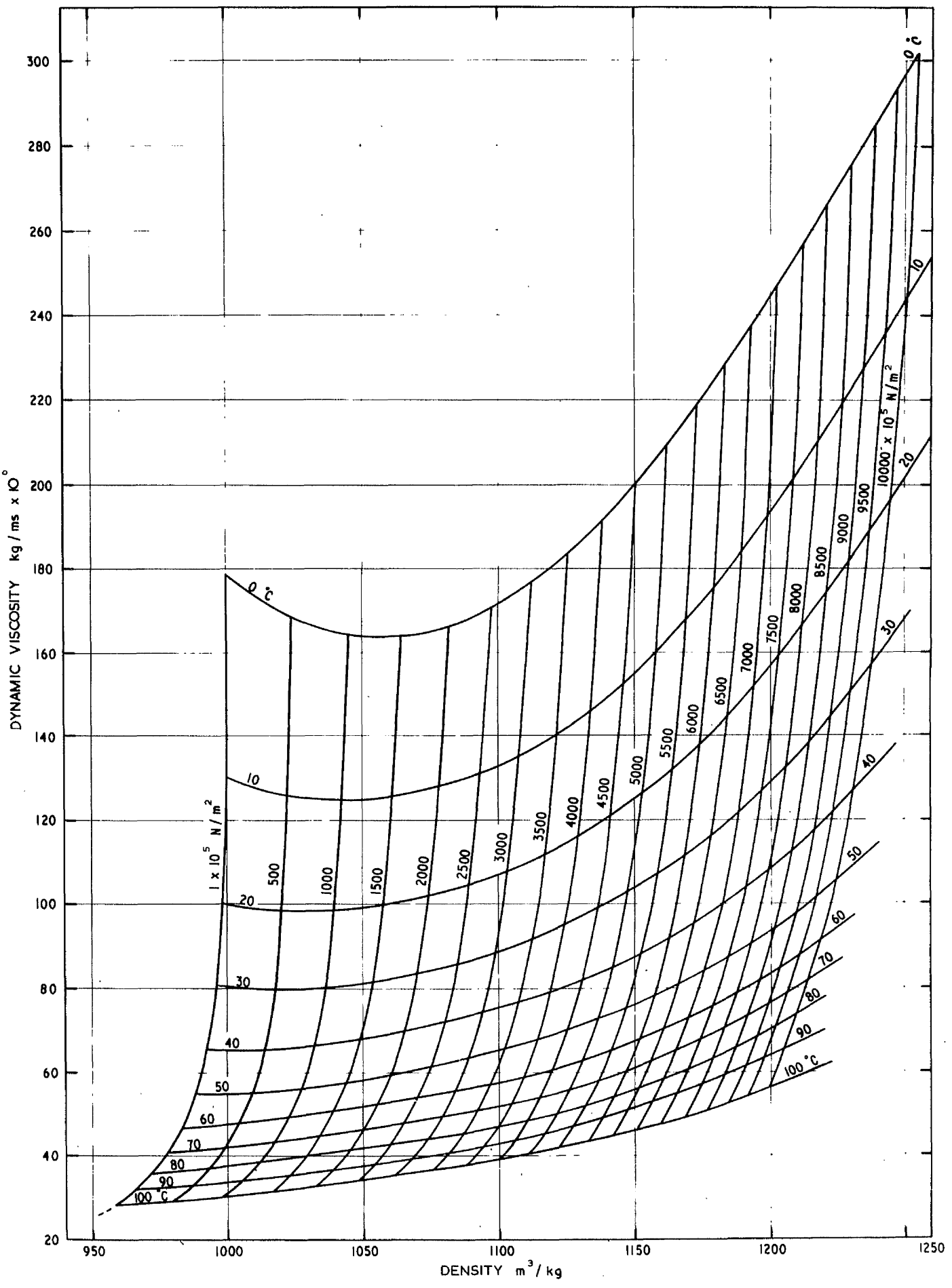

DYNAMIC VISCOSITY kg / ms x 10°
DENSITY m³ / kg
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
950
1000
1050
1100
1150
1200
1250
0 °C
10
20
30
40
50
60
70
80
90
100 °C
1 x 10⁵ N / m²
500
1000
1500
2000
2500
3000
3500
4000
4500
5000
5500
6000
6500
7000
7500
8000
8500
9000
9500
10000 x 10⁵ N / m²

Fig. 7

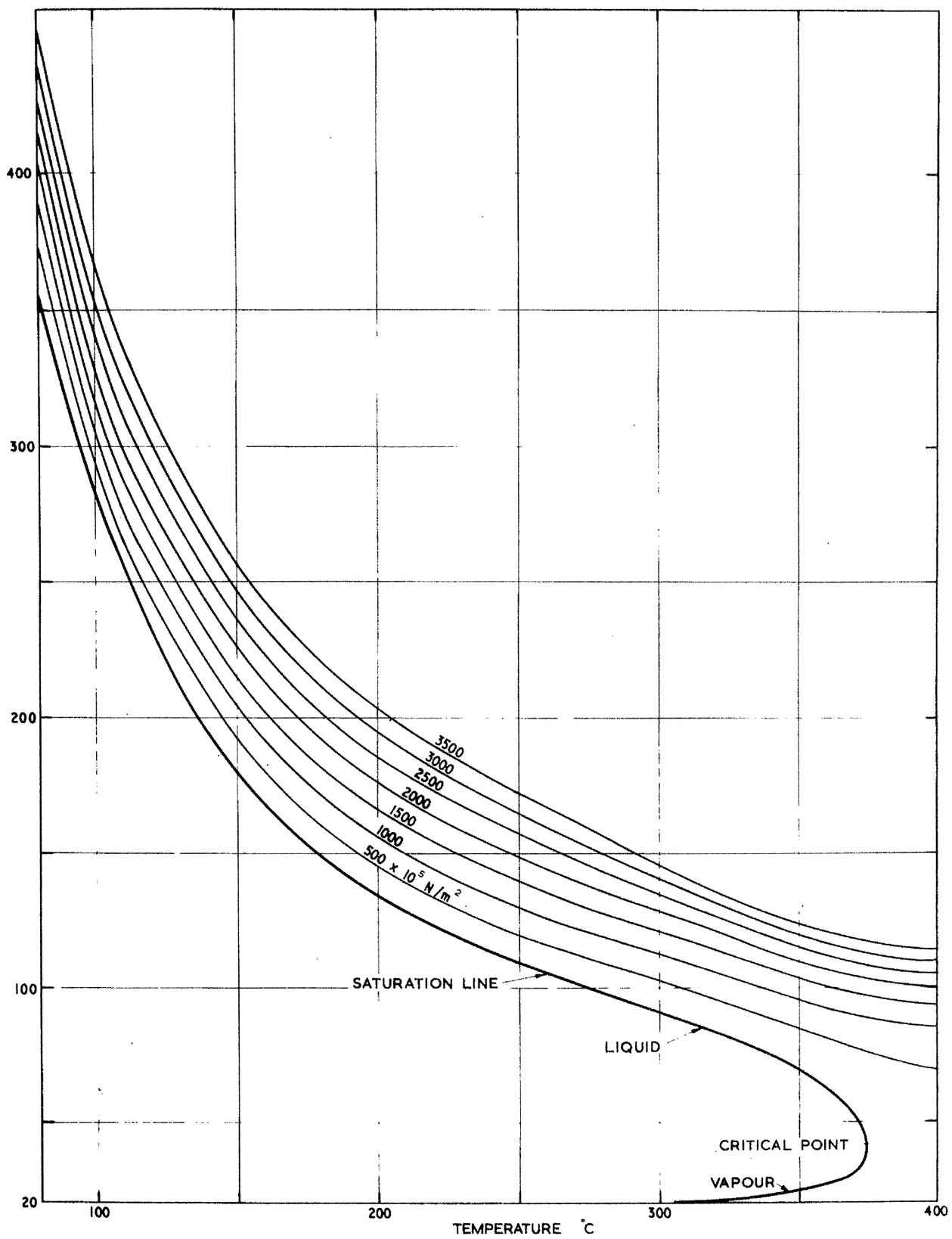

400
300
200
100
20
100
200
300
400
TEMPERATURE °C
3500
3000
2500
2000
1500
1000
500 x 10^5 N/m^2
SATURATION LINE
LIQUID
CRITICAL POINT
VAPOUR

Fig. 8

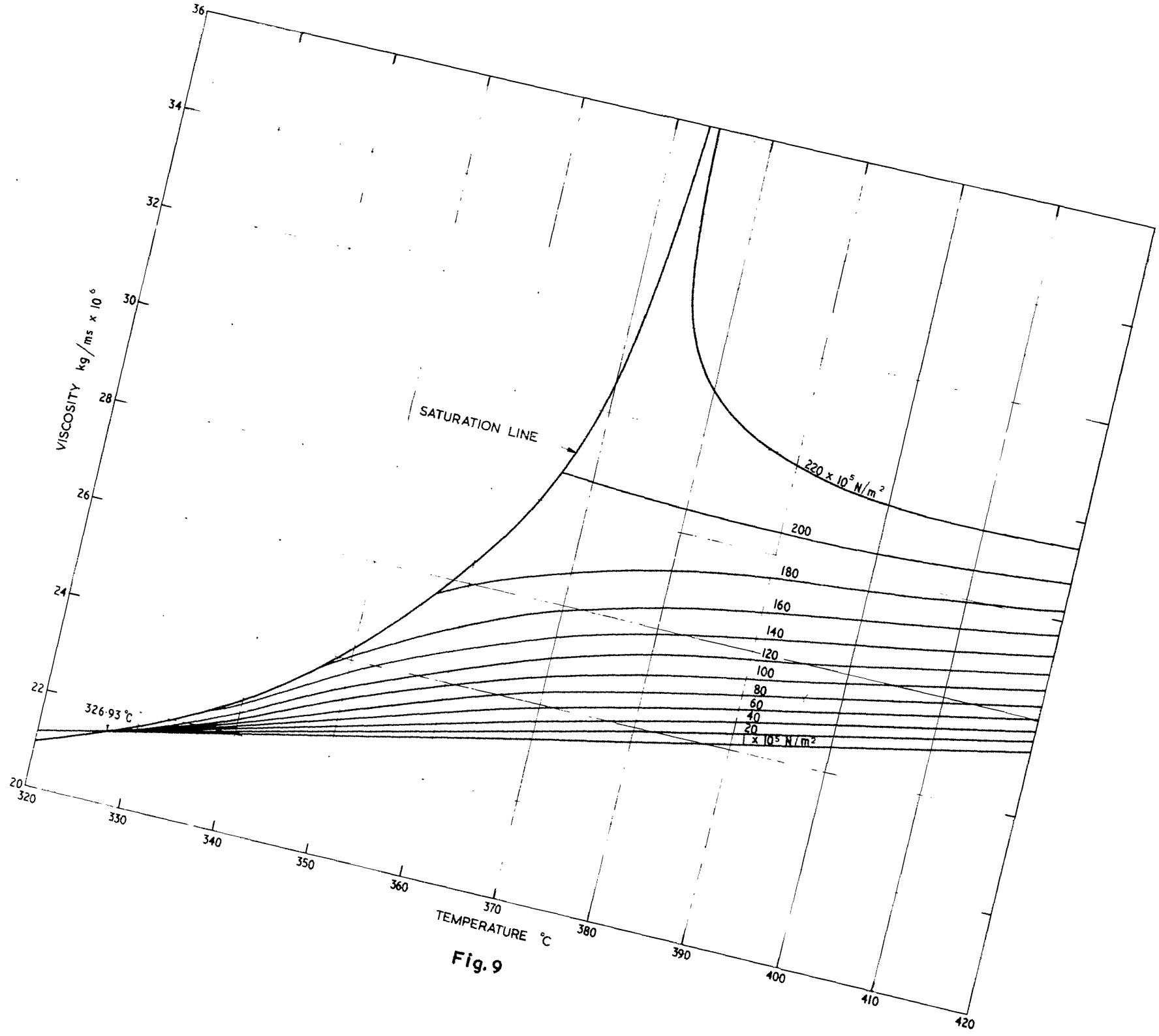

VISCOSITY kg/ms x 10⁶
36
34
32
30
28
26
24
22
20
SATURATION LINE
326·93 °C
220 x 10⁵ N/m²
200
180
160
140
120
100
80
60
40
20
x 10⁵ N/m²
320
330
340
350
360
370
380
390
400
410
420
TEMPERATURE °C

Fig. 9

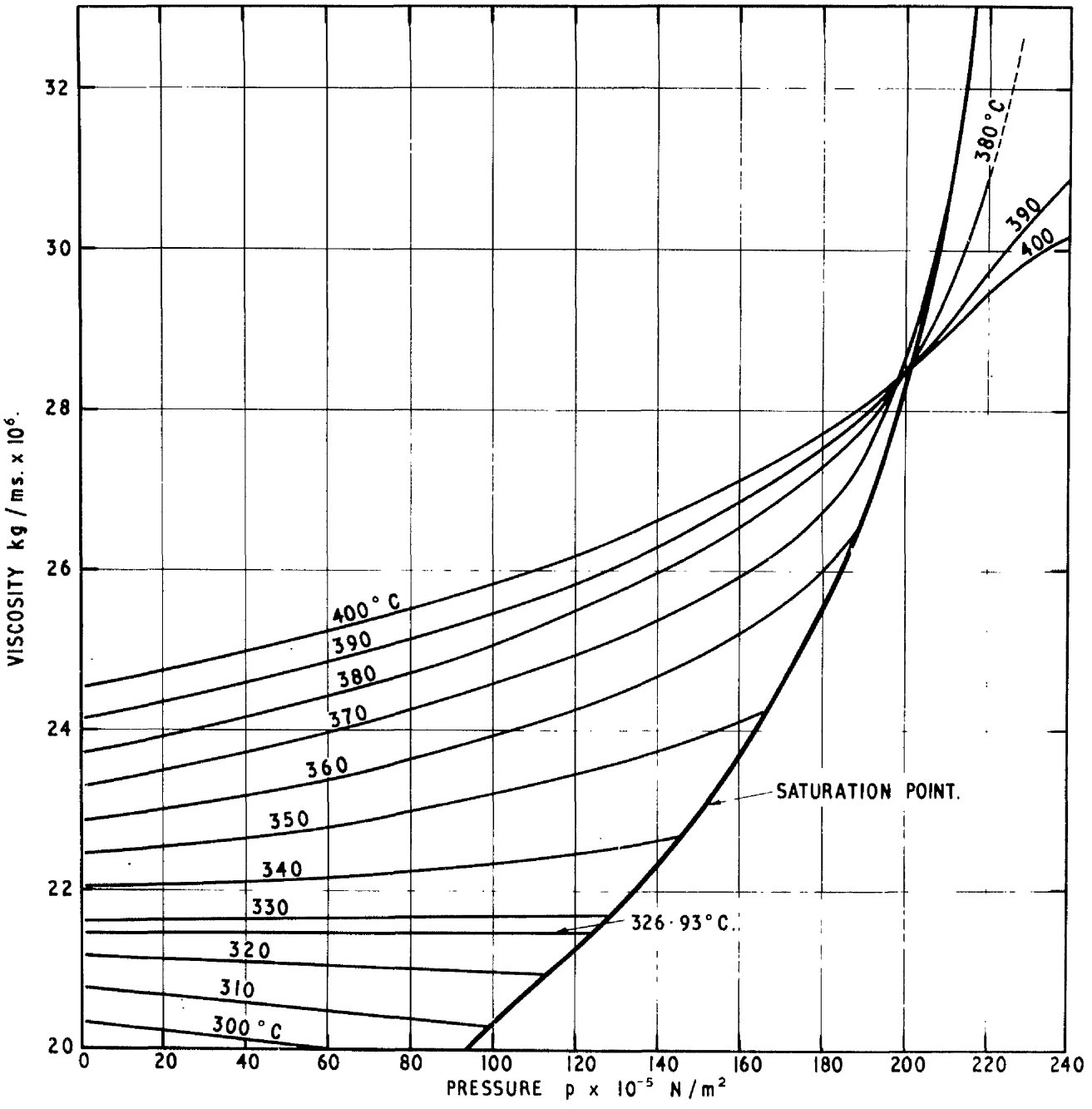

VISCOSITY kg / ms. x 10⁶.
32
30
28
26
24
22
20
0
20
40
60
80
100
120
140
160
180
200
220
240
PRESSURE p x 10⁻⁵ N / m²
400° C
390
380
370
360
350
340
330
320
310
300 °C
380°C
390
400
SATURATION POINT.
326·93°C.

Fig. 10

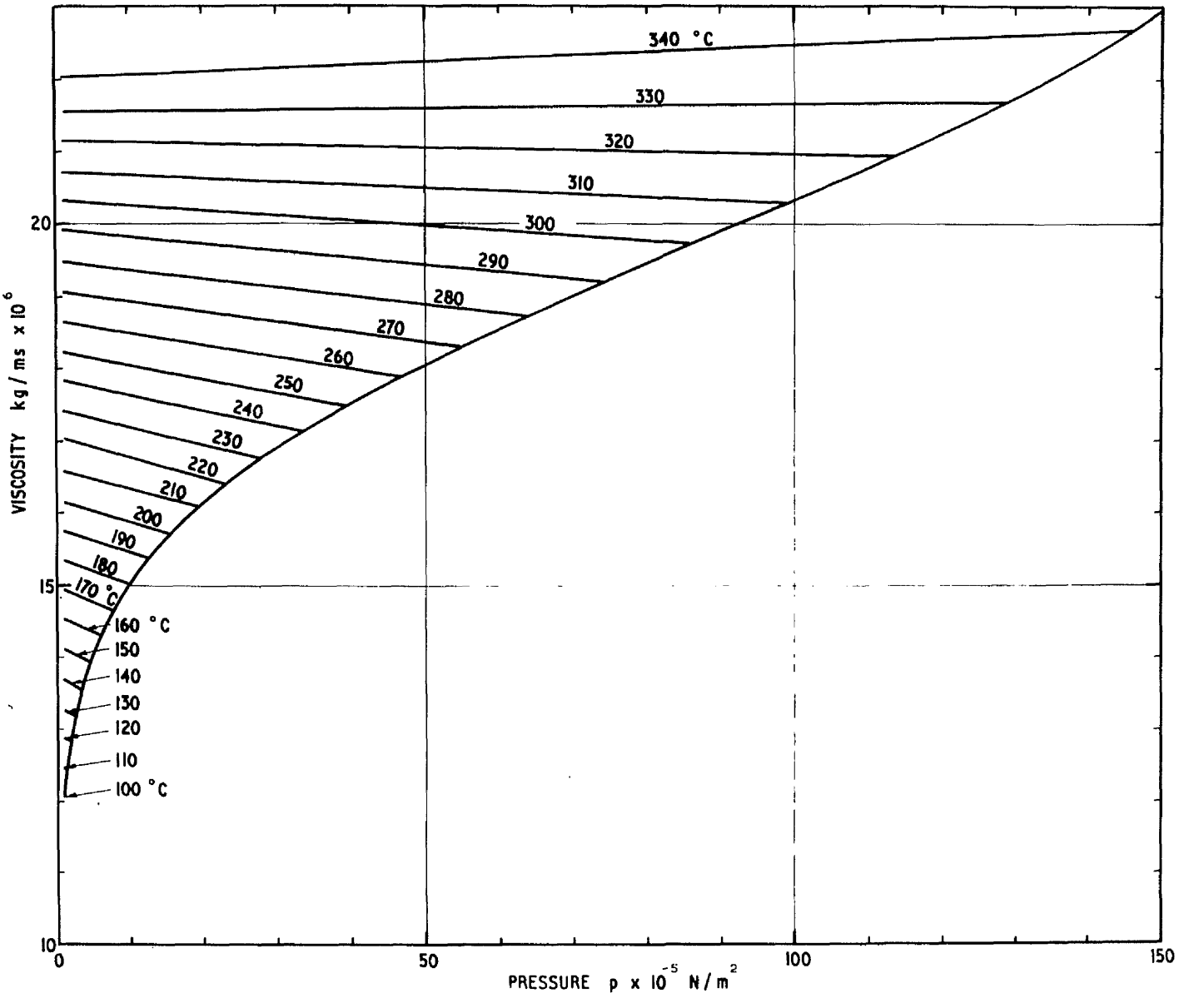

340 °C
330
320
310
300
290
280
270
260
250
240
230
220
210
200
190
180
170 °C
160 °C
150
140
130
120
110
100 °C
20
15
10
0
50
100
150
VISCOSITY kg/ms x 10^6
PRESSURE p x 10^-5 N/m^2

Fig. 11

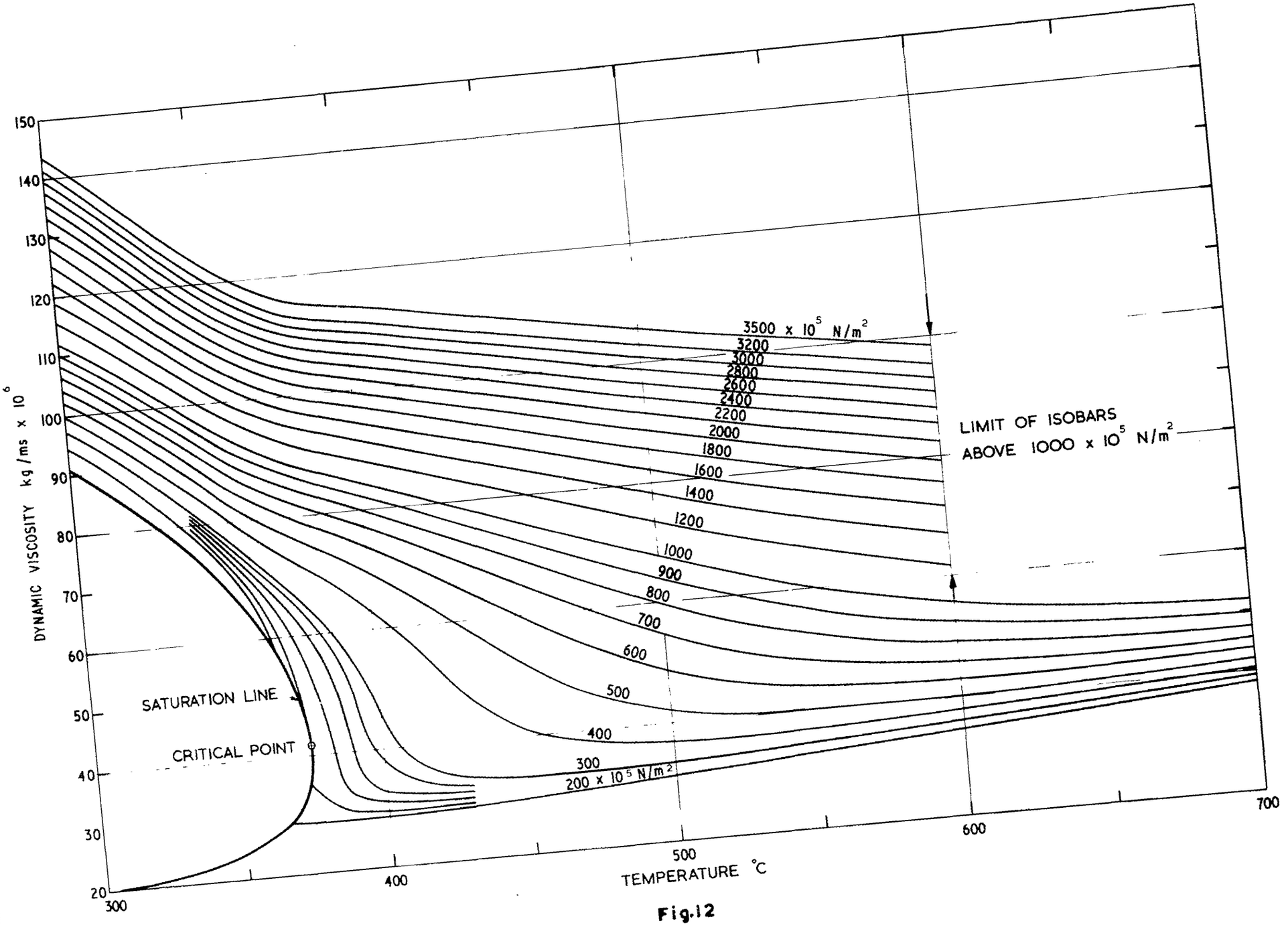

DYNAMIC VISCOSITY kg/ms x 10^6
150
140
130
120
110
100
90
80
70
60
50
40
30
20
300
400
500
600
700
TEMPERATURE °C
3500 x 10^5 N/m^2
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
900
800
700
600
500
400
300
200 x 10^5 N/m^2
LIMIT OF ISOBARS
ABOVE 1000 x 10^5 N/m^2
SATURATION LINE
CRITICAL POINT

Fig.12

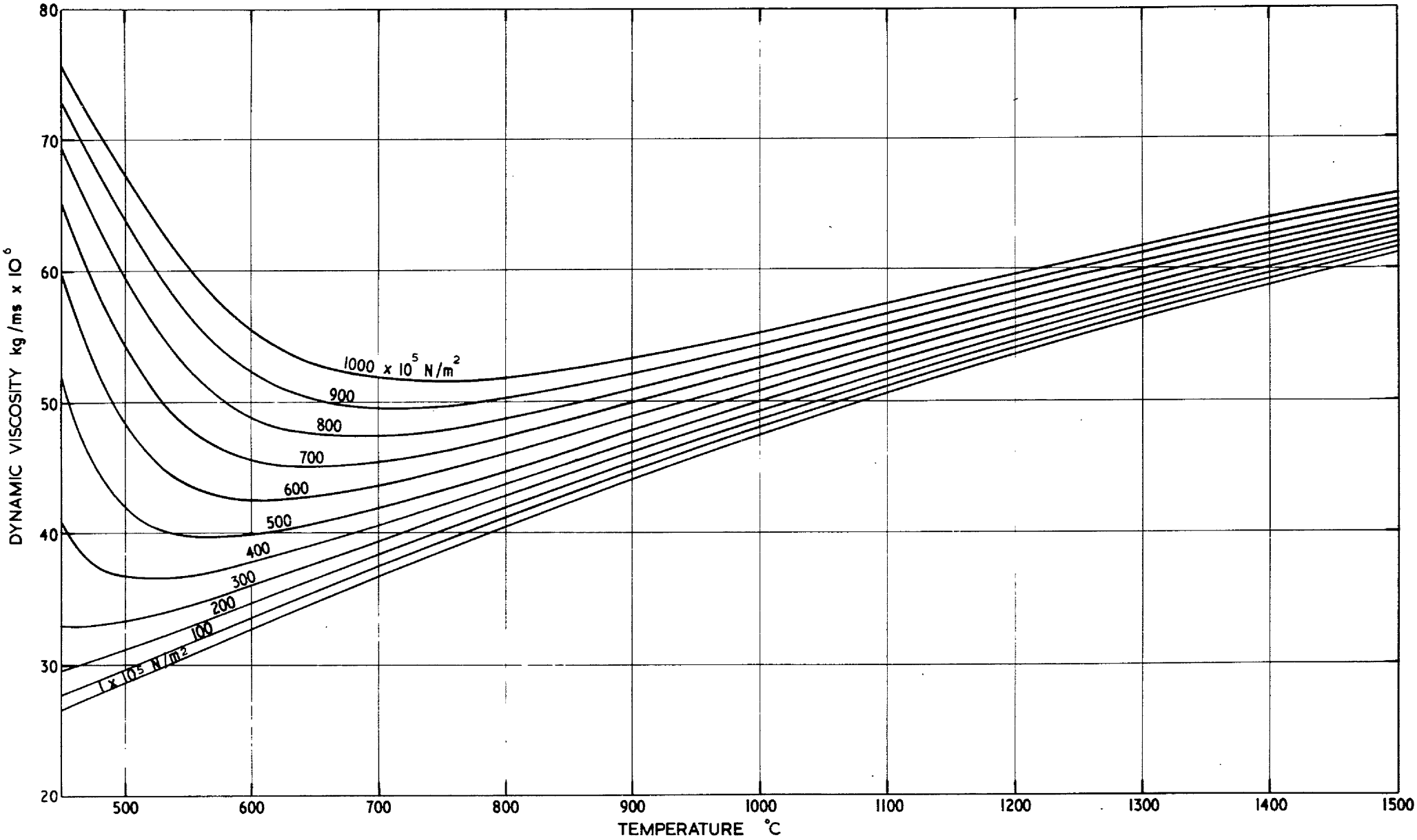

DYNAMIC VISCOSITY kg/ms x 10⁶
80
70
60
50
40
30
20
500
600
700
800
900
1000
1100
1200
1300
1400
1500
TEMPERATURE °C
1000 x 10⁵ N/m²
900
800
700
600
500
400
300
200
100
1 x 10⁵ N/m²

Fig. 13

APPENDIX

EQUATIONS FOR THE DYNAMIC VISCOSITY OF LIQUID AND GASEOUS H_2O

The following equations specify the dynamic viscosity (μ) of water and steam in Ns/m^2 where T is in ^oK, t in ^oC, p in N/m^2, ρ in kg/m^3. They give values which are within the tolerances of the International Skeleton Tables.

Several of the equations take the form of Chebyshev series where $T_m(x)$ is the Chebyshev polynomial of m th degree with x normalised in the range $-1 \leq x \leq 1$. The polynomials are calculated using a recurrence relation as follows:-

$$T_m(x) = 2xT_{m-1}(x) - T_{m-2}(x)$$
$$T_0(x) = 1$$
$$T_1(x) = x$$

Hence
$$T_2(x) = 2x^2 - 1$$
$$T_3(x) = 4x^3 - 3x \quad \text{etc.}$$

1 Water at atmospheric pressure

Equation (1) applies in the range $0^oC \leq t \leq 100^oC$

$$\mu = \sum_{m=0}^{8} a_m T_m(x) \qquad (1)$$

where $x = \left[2\left(\frac{T}{T_o}\right) - 2.36609921\right] / 0.36609921$ and the coefficients are

$a_0 = 7.654\ 497\ 35 \times 10^{-4}$
$a_1 = -6.628\ 585\ 16 \times 10^{-4}$
$a_2 = 2.408\ 023\ 47 \times 10^{-4}$
$a_3 = -7.973\ 601\ 35 \times 10^{-5}$
$a_4 = 2.541\ 962\ 82 \times 10^{-5}$
$a_5 = -8.059\ 669\ 31 \times 10^{-6}$
$a_6 = 2.589\ 903\ 20 \times 10^{-6}$
$a_7 = -8.329\ 834\ 33 \times 10^{-7}$
$a_8 = 2.751\ 794\ 88 \times 10^{-7}$.

2 Saturated liquid water

Equation (2) applies in the range $100\ ^oC \leq t \leq 350\ ^oC$

$$\mu_f = \sum_{m=0}^{5} b_m T_m(x) \qquad (2)$$

where $x = \left[2\left(\frac{T}{T_o}\right) - 3.7358594\right] / 1.0036610$ and the coefficients are

$b_0 = 1.381\ 879\ 27 \times 10^{-4}$
$b_1 = -9.908\ 862\ 92 \times 10^{-5}$
$b_2 = 2.640\ 790\ 92 \times 10^{-5}$
$b_3 = -1.533\ 888\ 02 \times 10^{-5}$
$b_4 = 2.421\ 351\ 63 \times 10^{-6}$
$b_5 = -1.622\ 637\ 68 \times 10^{-6}$

3 Compressed water

Equation (3.1) applies in the range $0\ ^oC \leq t \leq 100\ ^oC$ and $p_s \leq p \leq 10\ 000 \times 10^5\ N/m^2$ and in the range $100\ ^oC \leq t \leq 130\ ^oC$ and $p_s \leq p \leq 3500 \times 10^5\ N/m^2$

$$\mu = \mu_f + \sum_{i=0}^{5} \sum_{j=0}^{5} c_{ij} T_i(x) T_j(y) \qquad (3.1)$$

where $x = (\rho - \rho_s)\ 10^{-3} - 1$

$y = \frac{T - 373.15}{100}$.

Equation (3.2) applies in the range 130 °C $\leq$ t $\leq$ 300 °C and $p_s \leq p \leq 3500 \times 10^5$ N/m^2 and in the range 300 °C $\leq$ t $\leq$ 350 °C and $p_s \leq p \leq 1000 \times 10^5$ N/m^2

$$\mu = \mu_f + \sum_{i=0}^{4} \sum_{j=0}^{3} d_{ij} T_i(x) T_j(z) \qquad (3.2)$$

where $$z = \frac{T - 523.15}{150} .$$

The values of μ_f used are either equal to μ from equation (1) or μ_f from equation (2) depending on the temperature t. The coefficients c_{ij} and d_{ij} are tabulated below.

c_{ij} for Equation (31)

i \ j	0	1	2	3	4	5
0	$-8.86952796667 \times 10^{2}$	$-1.58730746282 \times 10^{3}$	$-1.16767754450 \times 10^{3}$	$-6.72988818200 \times 10^{2}$	$-2.82428614169 \times 10^{2}$	$-7.24067542375 \times 10^{1}$
1	$-1.49458041236 \times 10^{3}$	$-2.67469156898 \times 10^{3}$	$-1.96766399218 \times 10^{3}$	$-1.13415790410 \times 10^{3}$	$-4.75980307141 \times 10^{2}$	$-1.22076269753 \times 10^{2}$
2	$-8.82608875740 \times 10^{2}$	$-1.57944859821 \times 10^{3}$	$-1.16205738446 \times 10^{3}$	$-6.69982959275 \times 10^{2}$	$-2.81204030122 \times 10^{2}$	$-7.22076722920 \times 10^{1}$
3	$-3.49565860818 \times 10^{2}$	$-6.25518595616 \times 10^{2}$	$-4.60292172778 \times 10^{2}$	$-2.65497777658 \times 10^{2}$	$-1.11451090730 \times 10^{2}$	$-2.86764984400 \times 10^{1}$
4	-8.38157438965×10	$-1.49968961755 \times 10^{2}$	$-1.10380005371 \times 10^{2}$	-6.37069946172×10	-2.67481596837×10	-6.90238401943
5	-9.23114312350	-1.65148581921×10	-1.21587693674×10	-7.02309033384	-2.94940610307	$-7.64042355461 \times 10^{-1}$

c_{ij} for Equation(3.2)

i \ j	0	1	2	3
0	$-1.01002473749 \times 10^{-1}$	$3.31767627435 \times 10^{-1}$	$-1.02011451527 \times 10^{-1}$	$1.53747600990 \times 10^{-1}$
1	$-1.63630680052 \times 10^{-1}$	$5.36891946274 \times 10^{-1}$	$-1.64950137076 \times 10^{-1}$	$2.48931811588 \times 10^{-1}$
2	$-8.47399308460 \times 10^{-2}$	$2.77602513580 \times 10^{-1}$	$-8.51224304670 \times 10^{-2}$	$1.29014694813 \times 10^{-1}$
3	$-2.55383118217 \times 10^{-2}$	$8.37835630352 \times 10^{-2}$	$-2.56431741097 \times 10^{-2}$	$3.91761598633 \times 10^{-2}$
4	$-3.42658728002 \times 10^{-3}$	$1.13053682938 \times 10^{-2}$	$-3.45942919228 \times 10^{-3}$	$5.34567564729 \times 10^{-3}$

4 Superheated steam at low pressures

Equation (4) applies in the range 0 °C $\leq$ t $\leq$ 326.93 °C and $0 \leq p \leq 165 \times 10^5$ N/m^2.

$$\mu = a + b\left(\frac{T}{T_o}\right) + c\left(\frac{T}{T_o}\right)^2 - \frac{\rho}{\rho_c}\left\{d + e\left(\frac{T}{T_o}\right)\right\} \qquad (4)$$

where $a = -2.618\ 79 \times 10^{-6}$ $\quad d = 9.264\ 99 \times 10^{-5}$

$b = 1.052\ 82 \times 10^{-5}$ $\quad e = -4.217\ 33 \times 10^{-5}$

$c = 1.961\ 01 \times 10^{-7}$

5 Superheated steam at atmospheric pressure

Equation (5) applies in the range 326.93°C $\leq$ t $\leq$ 1000 °C and p = 1.01325x10^5 N/m^2.

$$\mu_1 = \sum_{i=0}^{4} f_i \left(\frac{T}{T_o}\right)^i \qquad (5)$$

where $f_0 = -1.194\ 705\ 8 \times 10^{-6}$ $\quad f_3 = -3.530\ 246\ 4 \times 10^{-7}$

$f_1 = 7.839\ 813\ 6 \times 10^{-6}$ $\quad f_4 = 1.765\ 5600 \times 10^{-8}$

$f_2 = 1.819\ 397\ 9 \times 10^{-6}$

Values may also be derived from equation (5) in the range 100°C $\leq$ t $\leq$ 326.93°C and will be found to differ by no more than 22×10^{-9} Ns/m^2 or about 0.1%. At 326.93°C equation (4) gives 21.457×10^{-6} Ns/m^2 and equation (5) gives 21.478×10^{-6} Ns/m^2.

6 Steam at supercritical temperatures

Equation (6) applies in the range 375 °C $\leq$ t $\leq$ 600 °C and 1.01325x10^5 N/m^2 and in the range 600 °C $\leq$ t $\leq$ 1000 °C and 1.01325x10^5 N/m^2 $\leq$ p $\leq$ 1000x10^5 N/m^2.

$$\mu = \mu_1 + m\left(\frac{\rho}{\rho_c}\right) + n\left(\frac{\rho}{\rho_c}\right)^2 \qquad (6)$$

where μ_1 is the dynamic viscosity at atmospheric pressure given by equation (5) and ρ density at pressure, p, and temperature T.

The values of the coefficients are

$m = 9.834\ 76 \times 10^{-6}$

and $n = 8.082\ 79 \times 10^{-6}$.

APPENDIX VI

The discontinuities exhibited by the equation of state for water substance devised by Juza

Juza's formulation covers the fluid from 100,000 bar to 1000 ^{o}C with four regions and it is important to confirm that the functions h, p and s are sufficiently smooth across the three inter-regional boundaries which are defined by the isochores v = 2.3256, 1.2658, 0.9524 cm^{3}/g. The adequacy of this formulation is shown in the accompanying table which gives the discontinuities recommended by the 1st IFC which were 0.005 p, 0.2 J/g and 0.0002 J/g K respectively. The only boundary where the recommended values are exceeded is in the range of temperature 255(t_s) $\leq$ t $\leq$ 272 ^{o}C.

Table of discontinuities

Boundary between Regions I and II

$t^{\circ}C$	p bar	dp	.0005 p	h J/g	dh	s J/g K	ds
1000	2806.3	.002645	1.40	4127.9	.000615	5.9285	.000000
800	2011.1	.002645	1.01	3501.2	.000615	5.5444	"
600	1174.5	.002645	.59	2789.1	.000615	5.0223	"
500	743.7	.002645	.37	2432.4	.000717	4.7099	
450	530.1	.002645	.27	2248.2	.000715	4.5299	"
400	323.7	.002594	.16	2051.3	.000697	4.3164	"
380	245.4	-.001440	.12	1966.9	-.000247	4.2166	"
375	226.7	.000809	.11	1946.4	.000272	4.1917	"
374	223.1	.002633	.11	1938.5	.000612	4.1810	"
373	219.6	.004004	.11	1933.4	.000931	4.1744	"
372	216.2	.002627	.11	1928.0	.000611	4.1673	"
371.5	214.5	-.000563	.11	1925.2	-.000131	4.1636	"
371.3	213.8	-.002612	.11	1924.0	-.000607	4.1620	"

Boundary between Regions II and III

1000	9097.6	-.005620	4.5	4267.2	-.001108	5.2501	.000000
800	6837.5	-.006650	3.4	3470.7	-.001275	4.8136	"
600	4473.6	-.008117	2.2	2647.6	-.001510	4.2728	"
500	3234.6	-.009096	1.6	2221.4	-.001663	3.9450	"
400	1947.8	-.0010289	.97	1782.3	-.001842	3.5623	"
300	621.6	.117417	.31	1323.7	.014313	3.0942	"
280	356.4	.117487	.18	1229.5	.014326	2.9865	"
260	94.1	.117195	.047	1134.2	.014298	2.8722	"
258	68.0	.117167	.034	1124.6	.014295	2.8604	"
256	42.1	.117138	.021	1115.0	.014293	2.8485	"

Boundary between Regions III and IV

1000	21433.5	.003366	10.7	5006.5	.000723	4.7837	.000000
800	17465.0	.003388	8.7	4095.6	.000752	4.3360	"
600	13334.1	.003374	6.7	3160.3	.000787	3.7765	"
400	9095.2	.003124	4.6	2187.7	.000815	3.0356	"
200	4698.4	.000904	2.3	1153.9	.000637	1.9485	"
0	1118.5	-.041505	.56	105.6	-.003885	-0.0125	-.000001

APPENDIX VII

An equation to represent the specific volume of water at atmospheric pressure, in the range 0 °C to 150 °C, as a function of temperature

This note which appeared as an appendix in reference (93), describes an equation which represents the 'atmospheric volume' of water as a function of temperature in the range 0 °C to 150 °C using a Chebyshev series. An equation, devised by Tilton and Taylor (97) already exists for calculating atmospheric density, but it is only valid in the range 0 °C to 45 °C.

Kell and Whalley (74), who have been making p-v-T measurements for water in the range 0 °C to 150 °C, produced an equation of the form

$$\frac{v}{v_A} = f\,(p,t) \qquad .....(161)$$

where v_A is the atmospheric volume.

They used Tilton and Taylor's equation from 0 °C to 45 °C, a table of v_A at 5 degree intervals from Owen, White and Smith (98) in the range 50 °C to 80 °C and their own measurements (74) of v_A at 5 degree intervals in the range 80 °C to 150 °C. The volumes above 100 °C are those for the metastable superheated liquid and not the volumes for the equilibrium state.

In order to make the use of equation (161) more straightforward, especially for the calculation of other properties by differentiation, it was decided to represent v_A by a single equation over the complete range. This would also ensure that v_A was absolutely smooth.

Using the values of v_A obtained from the above sources the following equation (162) was formulated to fit v_A to 1 p.p.m. up to 45 °C, to 2 p.p.m. up to 80 °C and to 3 p.p.m. up to 150 °C. The volumes obtained from equation (162) are tabulated at 5 degree intervals in the attached Table along with the differences, (v_A experimental - v_A equation (162) x 10^6), in parts per million.

$$v_A = \sum_{r=0}^{9} a_r T_r(x) \qquad .....(162)$$

where $x = t/75-1$.

The values of a_r are as follows:

$a_0 = 1.0353$
$a_1 = 4.5864\ 159_{10}-2$
$a_2 = 9.8033\ 008_{10}-3$
$a_3 = 5.1326\ 541_{10}-4$
$a_4 = 2.8558\ 355_{10}-4$
$a_5 = -5.7580\ 725_{10}-5$
$a_6 = 1.8096\ 991_{10}-5$
$a_7 = 4.8504\ 239_{10}-6$
$a_8 = 2.3814\ 401_{10}-6$
$a_9 = 1.5662\ 186_{10}-6$

Deviations and evaluation of equation (162) from original data

t	v_A Equation (162)	Difference
^oC	cm^3/g	p.p.m.
0	1.000160	0
5	1.000035	1
10	1.000300	0
15	1.000900	0
20	1.001797	0
25	1.002961	1
30	1.004367	1
35	1.005999	1
40	1.007841	0
45	1.009881	0
50	1.012108	-1
55	1.014514	-1
60	1.017091	0
65	1.019835	0
70	1.022740	2
80	1.029025	-1
85	1.032400	-2
90	1.035929	-1
95	1.039613	1
100	1.043450	0
105	1.047443	1
110	1.051592	1
115	1.055899	1
120	1.060336	-3
125	1.064996	2
130	1.069791	-1
135	1.074758	2
140	1.079901	-1
145	1.085225	1
150	1.090734	0

APPENDIX VIII

Summary of compressed water equations

v-p-t compressed water equation (154)

$$\frac{v}{v_A} = 1 + \sum_{i=0}^{5} \sum_{j=1}^{3} E_{ij}\, t^i (p-p_A)^j$$

$E_{01} = -5.09769\times10^{-5}$	$E_{02} = 8.2627\times10^{-9}$	$E_{03} = -9.109\times10^{-13}$
$E_{11} = 3.71999\times10^{-7}$	$E_{12} = -1.3794\times10^{-10}$	$E_{13} = 2.626\times10^{-14}$
$E_{21} = -7.01760\times10^{-9}$	$E_{22} = 3.4032\times10^{-12}$	$E_{23} = -8.913\times10^{-16}$
$E_{31} = 6.00227\times10^{-11}$	$E_{32} = -3.6432\times10^{-14}$	$E_{33} = 1.1467\times10^{-17}$
$E_{41} = -3.09041\times10^{-13}$	$E_{42} = 2.0836\times10^{-16}$	$E_{43} = -7.102\times10^{-20}$
$E_{51} = 5.93416\times10^{-16}$	$E_{52} = -4.1744\times10^{-19}$	$E_{53} = 1.4841\times10^{-22}$

h-p-s compressed water equation (155)

$$h = \sum_{i=0}^{4}{}' \sum_{j=0}^{3}{}' D_{ij}\, T_i(X) T_j(Y)$$

where $X = (2s - 11.99)/12.01$

and $Y = (2p-1000)/1000$

D_{ij}

i\j	0	1	2	3
0	$2.29396778966_{10}4$	$9.90221723853_{10}2$	$-9.22809517786_{10}1$	$3.44813660448_{10}0$
1	$1.49785098900_{10}4$	$7.05515999554_{10}2$	$-7.46436404816_{10}1$	$2.77856793062_{10}0$
2	$4.20456184702_{10}3$	$3.44974682900_{10}2$	$-3.93283089753_{10}1$	$1.44141411490_{10}0$
3	$6.47843041947_{10}2$	$9.93241195506_{10}1$	$-1.24112560347_{10}1$	$4.45137731177_{10}-1$
4	$4.47369162798_{10}1$	$1.36056524920_{10}1$	$-1.85857222935_{10}0$	$6.57125442419_{10}-2$

APPENDIX IX

Calculation of the efficiency of a water turbine

The efficiency of a water turbine or pump may be determined very elegantly by the 'thermodynamic method', a method which depends not only on the thermodynamic properties of water but also on the precision with which small temperature changes can be measured. Evaluation of the thermodynamic properties in such efficiency calculations may be carried out very easily using equation (155) and the following hypothetical results for a turbine are used to illustrate such an application.

The efficiency, η_{tu}, of a turbine is given by

$$\eta_{tu} = \frac{(h_1 - h_2)10^3 + g'(z_1 - z_2) + (V_1^2 - V_2^2)/2}{(h_p - h_2)_{s_p} 10^3 + g'(z_p - z_2) + (V_p^2 - V_2^2)/2} \qquad (163)$$

where the suffices refer to the measuring stations shown in the accompanying figure. In the example shown a small flow of water is taken from a point upstream of the turbine and throttled in a calorimeter. The temperature difference $(T_2 - T_1) = \Delta T$ is measured, from which observation the necessary fluid properties can be deduced. The following constants apply to the turbine for which the computed efficiencies are given in the table.

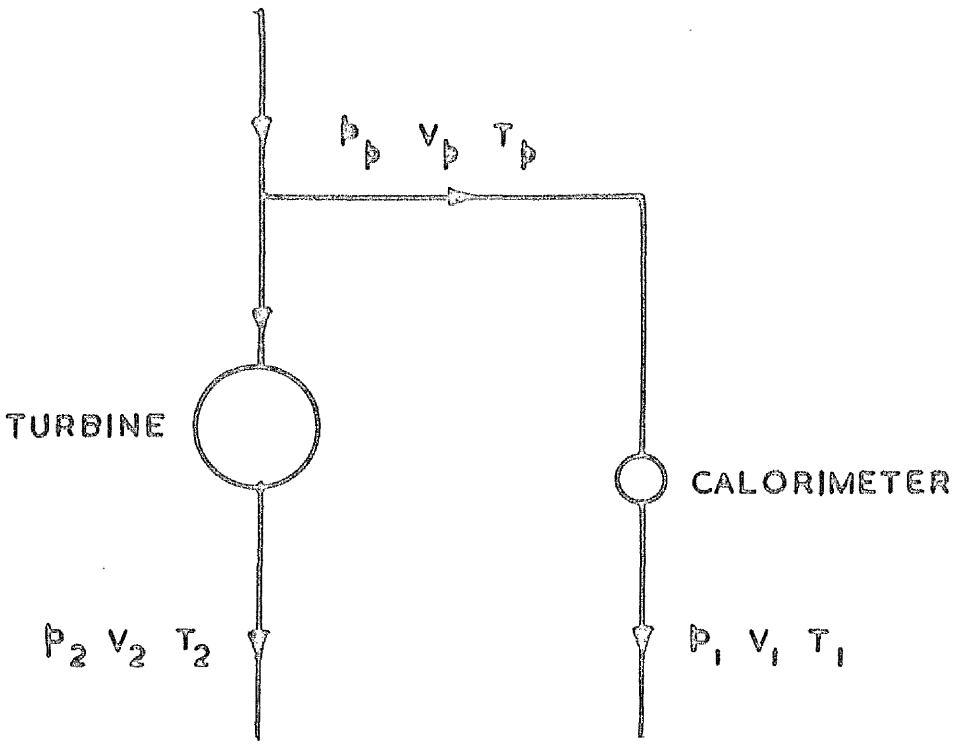
g'	9.798 m/s^2
z_1	479.2 m
z_2	476.9 m
z_p	481.8 m
V_1	0.5 m/s
V_2	5.2 m/s
V_p	zero (included in enthalpy term)
p_2	1.1 x 10^5 N/m^2
p_p	49.20 x 10^5 N/m^2
$T_1 = T_p = 10\ ^oC$	
$(h_1 - h_2)10^3$	enthalpy change J/kg
$(h_p - h_2)_s 10^3$	isentropic enthalpy change J/kg

$p_1 \times 10^{-5}$ N/m^2	$\Delta T \times 10^3$ °C	η_{tu} %		
		Thom's method	Eqn.(9)	Eqn.(10)
48.42	50.3	90.90	90.89	90.91
48.65	63.2	90.25	90.23	90.26
48.74	71.9	89.67	89.66	89.68
48.90	72.1	89.97	89.96	89.99
48.95	66.4	90.57	90.56	90.58
48.88	72.8	89.88	89.86	89.89
		Average 90.21	90.19	90.22

The efficiencies so derived are compared with the values which would have been obtained had the primary data, from which equation (155) was itself derived, been used instead. The efficiencies in the first column are derived by using certain coefficients described by Thom (99) where a full account of the 'thermodynamic method' is given. For the sake of completeness a revised set of coefficients, based on equation (154) is given here although the values differ only marginally from those quoted by Thom.

It is immediately seen from the above table that equation (155) gives values of η_{tu} in excellent agreement not only with whose which may be derived from the primary data of equation (154) but also with the values obtained by Thom's method. The authors would commend equation (155) to the practitioners of the thermodynamic method, of which group Thom is a member, together with the values of the coefficients given in Appendix III of reference (100). It is believed that considerable advantage would be derived by expressing all the quantities appearing in equation (163) in S.I. units as shown.

The calculation of pump efficiencies is carried out in an identical manner and for this reason it is not shown.



LAYOUT OF MEASURING STATIONS FOR A TURBINE

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Table 1

Differences between thermodynamic temperature and IPTS

temperature	Bridgeman & Aldrich		Ferguson	
^{o}C	$T - \tau$	$\frac{d\tau}{dT}$	$T - \tau$	$\frac{d\tau}{dT}$
0	0.0000	1.00047	0.0000	1.0004
100	-0.0060	0.99973	-0.0063	0.9997
200	0.0407	0.99942	0.0428	0.9994
300	0.0958	0.99955	0.0978	0.9996
374.15	0.1161	0.99994	0.1131	1.0000
400	0.1153	1.00013	0.1114	1.0001
500	-	-	0.0853	1.0002
600	-	-	0.1169	0.9987
700	-	-	0.5564	0.9955
800	-	-	0.8465	0.9983
900	-	-	0.9613	0.9990
1000	-	-	1.1201	0.9975

Table 2

Differences in saturation properties caused by incorrect use of the different temperature scales

t	$h_{f_{IST}}$	Tol	Δh_f	$v_{g_{IST}}$	Tol	Δv_g	β_1	$\Delta\beta_1$	s_f	Δs_f	s_g	Δs_g
°C	J/g			cm^3/g			J/g		J/g K		J/g K	
0	-0.0416	0.0004	0.000005	206288	210	-91	0.01212	0.000005	-0.0001	$2_{x10}{}^{-8}$	9.155	0
100	419.1	0.2	-0.0004	1673.0	1.7	0.5	1.40847	-0.0004	1.3069	0.00003	7.355	-0.0002
200	852.4	0.4	-0.009	127.19	0.13	0.06	17.81	-0.009	2.331	-0.0003	6.432	-0.0006
300	1345	1	-0.03	21.643	0.035	0.006	97.40	-0.03	3.255	-0.0008	5.705	-0.0007
374.15	2095	30	0.09	3.17	0.15	-0.0005	539.2	0.09	4.412	-0.0009	4.412	-0.001

Table 3

Differences in entropy and enthalpy caused by incorrect use of the different temperature scales

temperature °C	%Δs	pressure bar	h_{IST}	Tolerance J/g	Δh
0	0.044	1	0.06	0.01	$-2.4_{10}-6$
		200	20.1	0.4	$1.2_{10}-6$
		1000	95.7	1.2	$-1.2_{10}-4$
200	-0.058	1	2876	2	-0.18
		200	860.6	0.6	-0.05
		1000	903.8	1.5	-0.05
400	0.013	1	3278	3	0.17
		200	2819	8	0.11
		1000	1796	8	0.08
600	-0.13	1	3705	3	-0.95
		200	3538	10	-0.68
		1000	2861	10	-0.54
800	-0.17	1	4159	4	-0.93
		200	4065	11	-0.68
		1000	3715	20	-0.59

Table 4

Vapour entropy correlations

Equation	number of coefficients	k	maximum positive deviation J/g K	corresponding pressure bar	maximum negative deviation J/g K	corresponding pressure bar	maximum percentage deviation %	corresponding pressure bar	standard deviation J/g K
(i)	12	-	.4061	.7011	-.9188	.006112	-10.04	.006112	$2.47_{10}{}^{-1}$
(ii)	12	-	.2139	221.2	-.0478	203.11	4.855	221.2	$1.66_{10}{}^{-2}$
(iii)	12	.5	.0062	221.2	-.0101	220.86	-.225	220.86	$8.05_{10}{}^{-4}$
(iii)	10	.4	.0016	221.2	-.0040	220.86	-.088	220.86	$5.09_{10}{}^{-4}$
(iii)	10	.3	.0013	112.90	-.0021	193.60	-.042	193.60	$4.41_{10}{}^{-4}$
(iii)	10	.2	.0014	198.30	-.0018	193.60	-.036	193.60	$4.30_{10}{}^{-4}$
(iii)	11	.1	.0012	198.30	-.0018	193.60	-.035	193.60	$4.19_{10}{}^{-4}$

Table 5

Comparison of the entropy equation values with the NEL Table values

Temp. °C	Pressure bar	Liquid Entropy J/g K			Vapour Entropy J/g K		
		NEL Tables	Equation (133)	Deviation	NEL Tables	Equation (132)	Deviation
0	0.006107	-0.0002	-0.0002	0	9.155	9.155	0
0.01	0.006112	0.0000	0.0000	0	9.155	9.154	0.001
20	0.023368	0.2963	0.2964	-0.0001	8.666	8.666	0
40	0.073750	0.5721	0.5722	-0.0001	8.256	8.256	0
60	0.19919	0.8310	0.8310	0	7.909	7.908	0.001
80	0.47359	1.0752	1.0751	0.0001	7.611	7.611	0
100	1.01325	1.3069	1.3068	0.0001	7.355	7.355	0
120	1.9853	1.528	1.528	0	7.130	7.130	0
140	3.6136	1.739	1.739	0	6.930	6.931	-0.001
160	6.1805	1.942	1.943	-0.001	6.751	6.751	0
180	10.0271	2.139	2.139	0	6.586	6.586	0
200	15.551	2.331	2.331	0	6.431	6.432	-0.001
220	23.201	2.518	2.518	0	6.285	6.285	0
240	33.480	2.702	2.702	0	6.142	6.143	-0.001
260	46.940	2.885	2.885	0	6.001	6.001	0
280	64.192	3.068	3.068	0	5.857	5.857	0
300	85.92	3.255	3.255	0	5.705	5.705	0
320	112.90	3.449	3.449	0	5.535	5.536	-0.001
340	146.08	3.661	3.661	0	5.336	5.336	0
360	186.74	3.916	3.917	-0.001	5.053	5.053	0
370	210.52	4.114	4.114	0	4.795	4.796	-0.001
372	215.62	4.181	4.180	0.001	4.702	4.701	0.001
374	220.86	4.326	4.326	0	4.503	4.503	0
374.15	221.2	4.406	4.406	0	4.406	4.406	0

Table 6

Liquid entropy correlations

Equation	number of coefficients	k	maximum positive deviation J/g K	corresponding pressure bar	maximum negative deviation J/g K	corresponding pressure bar	maximum percentage deviation %	corresponding pressure bar	standard deviation J/g K
(i)	12	-	.6023	.006107	-.2937	.7849	$-3.01_{10}{}^{5}$	.006107	$1.74_{10}{}^{-1}$
(ii)	12	-	.0347	203.11	-.1603	221.2	$3.69_{10}{}^{3}$	.006107	$1.18_{10}{}^{-2}$
(iii)	12	.5	.0087	220.86	-.0053	221.2	$2.17_{10}{}^{2}$	.006107	$6.54_{10}{}^{-4}$
(iii)	12	.4	.0013	186.74	-.0011	215.63	$6.12_{10}{}^{1}$	.006107	$2.98_{10}{}^{-4}$
(iii)	9	.3	.0013	186.74	-.0010	193.60	$-6.97_{10}{}^{1}$	.006107	$2.89_{10}{}^{-4}$
(iii)	8	.2	.0012	186.74	-.0011	193.60	-8.99	.006107	$2.86_{10}{}^{-4}$
(iii)	10	.1	.0013	186.74	-.0010	193.60	$-6.08_{10}{}^{1}$	.006107	$2.87_{10}{}^{-4}$

Table 7

Vapour pressure correlations

Eqn	C	k	maximum positive deviation bar	corresponding temp. °C	maximum negative deviation bar	corresponding temp. °C	maximum percent deviation %	corresponding temp. °C	standard deviation bar
(iv)	-	-	.0240	374.15	-.0356	374	-64.68	0	3.23_{10}-3
(v)	-	-	.0268	374.15	-.0331	374	-.0150	374	2.59_{10}-3
(vi)	-	1	.0421	362	-.1197	374	-.0542	374	1.19_{10}-2
(vi)	-	.5	.0275	364	-.0788	374	.0357	374	7.16_{10}-3
(vi)	-	.4	.0259	364	-.0726	374	-.0329	374	6.47_{10}-3
(vi)	-	.3	.0228	365	-.0671	374	-.0301	374	5.85_{10}-3
(vii)	-	.5	.0120	373	-.0200	374	-.0091	374	1.62_{10}-3
(vii)	-	.4	.0093	374	-.0055	370	-.0063	0	1.16_{10}-3
(vii)	-	.3	.0234	373	-.0106	369	-.0107	373	2.19_{10}-3
(viii)	1	1	.0421	362	-.1197	374	-.0542	374	1.19_{10}-2
(viii)	1	.5	.0131	373	-.0097	374	.0060	373	1.31_{10}-3
(viii)	1	.4	.0095	374	-.0054	370	-.0064	0	1.17_{10}-3
(viii)	1	.3	.0236	373	-.0108	369	.0108	373	2.21_{10}-3
(viii)	1	.2	.0319	373	-.0252	371	.0146	373	3.65_{10}-3
(viii)	.8	.4	.0257	374.15	-.0342	374	-.0155	374	2.66_{10}-3
(viii)	.9	.4	.0336	374.15	-.0269	374	.0152	374.15	2.37_{10}-3
(viii)	.95	.4	.0347	374.15	-.0259	374	.0157	374.15	2.35_{10}-3
(viii)	.99	.4	.0265	374.15	-.0313	374	-.0142	374	2.32_{10}-3

Table 8

Vapour pressure derivatives at the critical point

p-t equation		t-p equation	
C	$(T\frac{dp}{dT})_{crit}$ (J/cm^3)	K	$(T\frac{dp}{dT})_{crit}$ (J/cm^3)
.8	170.97	1.4	171.05
.85	171.10	1.3	171.29
.9	171.24	1.2	171.39
.95	171.27	1.1	170.33
.99	170.00	1.001	139.33
.995	168.70	1.0001	96.90
.9995	156.21	1.000001	20.15
.9999	120.44	1	0
1	0		

Table 9

Comparison of vapour pressure equation with 1963 IST

temp. °C	pressure, bar		
	IST	Equation (137)	$(p_{EQN} - p_{IST})$/Tolerance
0	.006108	.006107	-1/6
0.01	.006112	.006112	0/6
10	.012271	.012271	0/10
20	.023368	.023368	0/20
30	.042418	.042417	1/30
40	.073750	.073749	1/38
50	.12335	.12335	0/6
60	.19919	.19919	0/10
70	.31161	.31161	0/16
80	.47358	.47359	-1/24
90	.70109	.70108	1/36
100	1.01325	1.01325	0/*
110	1.4327	1.4326	1/10
120	1.9854	1.9854	0/13
130	2.7011	2.7012	-1/16
140	3.6136	3.6136	0/21
150	4.7597	4.7597	0/32
160	6.1804	6.1804	0/42
170	7.9202	7.9202	0/53
180	10.027	10.027	0/7
190	12.553	12.552	1/8
200	15.550	15.550	0/8
210	19.080	19.080	0/8
220	23.202	23.201	1/9
230	27.979	27.979	0/10
240	33.480	33.480	0/12
250	39.776	39.776	0/13
260	46.941	46.940	1/15
270	55.052	55.051	1/17
280	64.191	64.191	0/20
290	74.449	74.448	1/22
300	85.917	85.917	0/24
310	98.694	98.696	-2/30
320	112.89	112.90	-1/3
330	128.65	128.65	0/4
340	146.08	146.08	0/4
350	165.37	165.37	0/4
360	186.74	186.74	0/5
370	210.53	210.53	0/5
371	213.06	213.06	0/10
372	215.63	215.62	1/11
373	218.2	218.21	-.1/1
374	220.9	220.84	.6/1
374.15	221.2	221.23	-.3/1

Table 10

Supplementary equation correlations

K	k	maximum positive deviation deg C	corresponding pressure bar	maximum negative deviation deg C	corresponding pressure bar	maximum percentage deviation %	corresponding pressure bar	standard deviation deg C
1	.5	.0046	220.86	-.0045	218.22	$7.10_{10}-4$	220.86	$5.47_{10}-4$
1	.4	.0027	208.02	-.0038	218.22	$-5.96_{10}-4$	218.22	$8.17_{10}-4$
1	.3	.0027	208.02	-.0051	218.22	$-7.93_{10}-4$	218.22	$8.46_{10}-4$
1	.2	.0077	213.06	-.0094	218.22	$-1.46_{10}-3$	218.22	$1.73_{10}-3$
10	.4	.0148	220.86	-.0079	221.2	$2.28_{10}-3$	220.86	$1.29_{10}-3$
1.4	.4	.0091	220.86	-.0139	221.2	$-2.15_{10}-3$	221.2	$9.03_{10}-4$
1.1	.4	.0115	220.86	-.0108	221.2	$1.77_{10}-3$	220.86	$8.97_{10}-4$
1.05	.4	.0121	220.86	-.0093	221.2	$1.88_{10}-3$	220.86	$9.51_{10}-4$

Table 11

Use of primary and supplementary equations in conjunction

temperature °C	pressure bar	temperature °C
0	.006107	0.0006
20	.023368	20.0005
40	.073749	40.0005
60	.19919	60.0004
80	.47359	80.0005
100	1.01325	100.0006
120	1.9854	120.0006
140	3.6136	140.0002
160	6.1804	159.9999
180	10.027	179.9999
200	15.551	200.0001
220	23.201	220.0002
240	33.480	240.0000
260	46.940	259.9994
280	64.191	279.9992
300	85.917	299.9999
320	112.90	320.0002
340	146.08	339.9987
360	186.74	360.0008
370	210.53	369.998
372	215.62	371.997
374	220.84	374.001
374.15	221.23	374.152

Table 12

Use of supplementary and primary equations in conjunction

pressure bar	temperature °C	pressure bar
.01	6.9826	.0100004
.05	32.898	.0500014
.1	45.834	.100002
.5	81.346	.500010
1.	99.632	1.00002
5.	151.85	5.00000
10.	179.88	9.99997
50.	263.92	49.9995
100.	310.96	100.0004
150	342.12	149.997
200.	365.71	200.002
220	373.68	219.999
221.2	374.14	221.205

Table 13

Comparison of the vapour pressure equations (137) and (137b) with API 44

Temperature	pressure, bar		
°C	API 44	equation (137b)	equation (137)
0	.006107	.006107	.006107
0.1	.006112	.006112	.006112
20	.023379	.023379	.023368
40	.073773	.073774	.073749
60	.19924	.19924	.19919
80	.47364	.47364	.47359
100	1.01325	1.01325	1.01325
120	1.9853	1.9853	1.9854
140	3.6136	3.6135	3.6136
160	-	6.1805	6.1804
180	-	10.027	10.027
200	-	15.551	15.551
220	-	23.201	23.201
240	-	33.480	33.480
260	-	46.940	46.940
280	-	64.192	64.191
300	-	85.916	85.917
320	-	112.90	112.90
340	-	146.08	146.08
360	-	186.74	186.74
370	-	210.53	210.53
371	-	213.06	213.06
372	-	215.62	215.62
373	-	218.21	218.21
374	-	220.84	220.84
374.15	-	221.23	221.23

Table 14

Comparison of the derivatives from equations (137) and (137b) with API 44

Temperature	pressure, bar		
^{o}C	API 44	equation (137b)	equation (137)
0	.012137	.012140	.012121
10	.023293	.023291	.023277
20	.042435	.042437	.042424
40	.12315	.12314	.12311
60	.30720	.30719	.30715
80	.67736	.67738	.67741
100	1.3499	1.3497	1.3498
120	2.4728	2.4729	2.4729
140	4.2256	4.2257	4.2255
160	-	6.8117	6.8115
180	-	10.455	10.455
200	-	15.395	15.396
220	-	21.889	21.889
240	-	30.207	30.206
260	-	40.649	40.648
280	-	53.565	53.565
300	-	69.386	69.389
320	-	88.694	88.694
340	-	112.39	112.38
360	-	142.51	142.52
370	-	161.85	161.83
371	-	164.03	164.02
372	-	166.27	166.25
373	-	168.56	168.55
374	-	170.92	170.91
374.15	-	171.28	171.27

Table 15

Criteria for judging equations

Equation	min. t °C	max. t °C	No. of coeffs.	Number of operations					Total time as multiples of +
				+	X	/	ln, exp	↑	
OSG	0	100	5	4	3	2	1	1	80
	100	374.11	10	6	8	2	-	3	152
SS	10	93	4	4	8	2	-	1	70
	93	373.9	6	5	9	2	-	1	73
BA	0	374.15	14	12	15	3	-	1	97 (also contains $\cosh^{-1}$)
1966 K	0	374.15	12	10	12	2	4	1	164
1967 K	0	374.15	8	8	10	2	1	-	58
equation (137)	0	374.15	16	28	15	1	1	1	123

Table 16

Algol time factors on the KDF 9

	Operation		time factor
addition subtraction	a+b	+	1
multiplication	axb	x	2
division	a/b	/	5
logarithm exponential		ln,exp	20
power	a^b	↑	40

Table 17

Times for evaluating the vapour pressure equations

Formula	U/CODE STORAGE IN WORDS	AVE. TIME MILLI-SECONDS	
		U/CODE	ALGOL
1966 K Function	36	2.47	3.89
1967 K Function	23	0.92	1.43
Equation (137)	38	2.10	5.46

Table 18

Comparison of vapour pressure equations

temperature	pressure, bar					
°C	O S G	S S	B A	1966 K function	1967 K function	equation (137)
0	.006108	-	.006108	.006108	.006108	.006107
0.01	.006112	-	.006112	.006112	.006112	.006112
20	.023368	.023376	.023373	.023371	.023366	.023368
40	.073750	.073743	.073779	.073743	.073750	.073749
60	.19919	.11916	.11927	.19919	.19920	.19919
80	.47358	.47353	.47367	.47361	.47360	.47359
100	1.01325	1.01325	1.01325	1.01325	1.01325	1.01325
120	1.9854	1.9855	1.9853	1.9853	1.9854	1.9854
140	3.6136	3.6141	3.6134	3.6135	3.6138	3.6136
160	6.1804	6.1815	6.1804	6.1804	6.1806	6.1804
180	10.027	10.029	10.027	10.027	10.027	10.027
200	15.550	15.552	15.551	15.550	15.549	15.551
220	23.202	23.202	23.201	23.201	23.198	23.201
240	33.480	33.479	33.480	33.480	33.478	33.480
260	46.941	46.947	46.939	46.940	46.943	46.940
280	64.191	64.185	64.190	64.192	64.202	64.191
300	85.917	85.903	85.915	85.917	85.927	85.917
320	112.89	112.87	112.90	112.90	112.89	112.90
340	146.08	146.04	146.08	146.08	146.05	146.08
360	186.74	186.72	186.73	186.73	186.75	186.74
370	210.53	210.49	210.52	210.50	210.54	210.53
371	213.06	213.02	213.07	213.02	213.06	213.06
372	215.63	215.57	215.63	215.58	215.62	215.62
373	218.23	218.16	218.22	218.18	218.20	218.21
374	220.87	-	220.86	220.80	220.81	220.84
374.15	221.29	-	221.25	221.20	221.20	221.23

Table 19

Comparison of derivatives from the vapour pressure equations

temperature	$T\frac{dp}{dT}$, J/cm^3						
°C	O S C	S S	B A	1966 K function	1967 K function	equation (137)	equation (138)
0	.012122	-	.012120	.012147	.012118	.012121	.012121
10	.023277	.023274	.023278	.023279	.023272	.023277	.023277
20	.042424	.042412	.042430	.042410	.042421	.042424	.042424
40	.12311	.12308	.12311	.12310	.12312	.12311	.12311
60	.30715	.30711	.30711	.30718	.30717	.30715	.30716
80	.67743	.67742	.67723	.67743	.67740	.67741	.67741
100	1.3497	1.3499	1.3495	1.3497	1.3498	1.3498	1.3498
120	2.4729	2.4735	2.4728	2.4728	2.4732	2.4729	2.4730
140	4.2255	4.2267	4.2259	4.2255	4.2258	4.2255	4.2256
160	6.8116	6.8130	6.8122	6.8115	6.8110	6.8115	6.8115
180	10.455	10.456	10.455	10.455	10.453	10.455	10.455
200	15.396	15.395	15.395	15.396	15.392	15.396	15.396
220	21.889	21.886	21.887	21.889	21.888	21.889	21.889
240	30.206	30.202	30.205	30.208	30.214	30.206	30.207
260	40.649	40.644	40.649	40.657	40.667	40.648	40.649
280	53.565	53.553	53.568	53.597	53.581	53.565	53.564
300	69.386	69.356	69.389	69.497	69.364	69.389	69.386
320	88.692	88.642	88.691	89.043	88.616	88.694	88.697
340	112.39	112.39	112.39	113.36	112.39	112.38	112.39
350	126.40	126.48	126.41	127.90	126.54	126.41	126.39
360	142.49	142.59	142.51	144.59	142.71	142.52	142.49
365	151.65	151.62	151.67	153.97	151.71	151.67	151.71
370	161.94	161.48	161.97	164.22	161.44	161.83	161.96
371	164.21	163.56	164.24	166.40	163.48	164.02	164.10
372	166.60	165.69	166.57	168.63	165.55	166.25	166.22
373	169.19	167.86	169.01	170.91	167.66	168.55	168.26
374	172.53	-	171.57	173.27	169.81	170.91	170.11
374.15	173.13	-	171.91	173.63	0	171.27	170.36

Table 20

Liquid volume correlations

Equn.	k	maximum positive deviation cm^3/g	corresponding t °C	maximum negative deviation cm^3/g	corresponding t °C	maximum percentage deviation %	corresponding t °C	standard deviation cm^3/g
(x)	.4	.00190	372	-.00137	366	-.080	372	$3.13_{10}-2$
(x)	.3	.00126	372	-.00110	366	-.058	335	$2.12_{10}-2$
(xi)	.4	.00998	374	-.00818	373	.357	374	$1.02_{10}-1$
(xi)	.3	.00137	357	-.00117	335	.075	357	$2.72_{10}-2$
(xii)	.4	.00158	372	-.00158	372	.066	372	$2.20_{10}-4$
(xii)	.3	.00200	372	-.00238	373	-.095	373	$2.66_{10}-4$
(xiii)	.4	.00999	374	-.00496	373	.357	374	$7.35_{10}-4$
(xiii)	.3	.00348	373	-.00184	369	.139	373	$3.92_{10}-4$

Table 21

Comparison of liquid volume equation with 1963 IST

temperature	liquid volume, cm^3/g		
°C	IST	Equation (139)	Δv /Tolerance
0	1.00021	1.00018	3/5
0.01	1.00021	1.00018	3/5
10	1.0004	1.0004	0/1
20	1.0018	1.0018	0/1
30	1.0044	1.0044	0/1
40	1.0079	1.0078	1/1
50	1.0121	1.0121	0/2
60	1.0171	1.0171	0/2
70	1.0228	1.0227	1/2
80	1.0290	1.0290	0/3
90	1.0359	1.0360	-1/3
100	1.0435	1.0435	0/3
110	1.0515	1.0516	-1/4
120	1.0603	1.0603	0/4
130	1.0697	1.0697	0/4
140	1.0798	1.0798	0/4
150	1.0906	1.0905	1/4
160	1.1021	1.1020	1/4
170	1.1144	1.1143	1/4
180	1.1275	1.1274	1/4
190	1.1415	1.1415	0/4
200	1.1565	1.1565	0/4
210	1.1726	1.1727	-1/4
220	1.1900	1.1901	-1/4
230	1.2087	1.2088	-1/4
240	1.2291	1.2291	0/4
250	1.2512	1.2512	0/4
260	1.2755	1.2754	1/4
270	1.3023	1.3022	1/4
280	1.3321	1.3320	1/4
290	1.3655	1.3655	0/5
300	1.4036	1.4036	0/7
310	1.4475	1.4477	-2/7
320	1.4992	1.4995	-3/7
330	1.562	1.562	0/1
340	1.639	1.639	0/1
350	1.741	1.741	0/1
360	1.894	1.893	1/4
370	2.22	2.22	0/2
371	2.29	2.29	0/2
372	2.38	2.38	0/3
373	2.51	2.51	0/4
374	2.80	2.80	0/15
374.15	3.17	3.15	2/15

Table 22

α correlations

k	C	maximum positive deviation J/g	corresponding t °C	maximum negative deviation J/g	corresponding t °C	maximum percentage deviation %	corresponding t °C	standard deviation cm^3/g
.5	1	.0078	374	-.0078	108	7.4	.01	.0031
.4	1	.0069	136	-.0080	108	10.1	.01	.0030
.3	1	.0284	373	-.0134	366	42.5	.01	.0064
.5	.99	.0067	136	-.0068	108	0.46	.01	.0028
.5	.95	.0059	136	-.0064	108	4.4	.01	.0027
.5	.9	.0058	136	-.0065	108	5.7	.01	.0027

Table 23

Comparison of β' from saturation equations with NBS values

temperature °C	β', J/g		$\Delta\beta'$ J/g
	OSG	saturation equations	
0	0.0121	0.0121	0
20	0.0425	0.0425	0
40	0.1241	0.1241	0
60	0.3124	0.3124	0
80	0.6971	0.6971	0
100	1.4084	1.4085	0.0001
120	2.62	2.62	0
140	4.56	4.56	0
160	7.51	7.51	0
180	11.79	11.79	0
200	17.80	17.81	0.01
220	26.04	26.05	0.01
240	37.13	37.13	0
260	51.85	51.85	0
280	71.35	71.35	0
300	97.39	97.39	0
320	132.96	133.00	0.04
340	184.25	184.20	-0.05
360	269.85	269.85	0
370	360.30	360.13	-0.17
372	396.66	395.94	-0.72
374	483.57	478.53	-5.04
374.15	535.2	539.1	3.9

Table 24

Comparison of liquid enthalpy from saturation equations with 1963 IST

temperature	liquid enthalpy, J/g		
°C	IST	saturation equations	Δ h/Tolerance
0	-0.0416	-0.0416	0/4
0.01	.000611	.000611	0/1
10	41.99	42.00	-1/4
20	83.86	83.86	0/8
30	125.66	125.66	0/8
40	167.47	167.45	2/8
50	209.3	209.3	0/1
60	251.1	251.1	0/1
70	293.0	293.0	0/1
80	334.9	334.9	0/2
90	376.9	376.9	0/2
100	419.1	419.1	0/2
110	461.3	461.3	0/2
120	503.7	503.7	0/2
130	546.3	546.3	0/3
140	589.1	589.1	0/3
150	632.2	632.1	1/3
160	675.5	675.5	0/3
170	719.1	719.1	0/4
180	763.3	763.1	2/4
190	807.5	807.5	0/4
200	852.4	852.3	1/4
210	897.7	897.7	0/4
220	943.7	943.7	0/4
230	990.3	990.3	0/5
240	1037.6	1037.6	0/5
250	1085.8	1085.8	0/5
260	1135.0	1135.9	1/7
270	1185.2	1185.2	0/8
280	1236.8	1236.8	0/8
290	1290	1290	0/1
300	1345	1345	0/1
310	1402	1402	0/2
320	1462	1462	0/2
330	1526	1526	0/2
340	1596	1595	1/3
350	1672	1671	1/3
360	1762	1762	0/3
370	1892	1892	0/6
371	1913	1912	1/6
372	1937	1936	1/9
373	1969	1967	2/14
374	2032	2027	5/20
374.15	2095	2088	7/30

Table 25

Comparison of liquid entropy from saturation equations with NEL Table values

temperature °C	s_f, J/g K		Δs_f J/g K
	NEL Tables	saturation equations	
0	-0.0002	-0.0001	0.0001
20	0.2963	0.2963	0
40	0.5721	0.5721	0
60	0.8310	0.8310	0
80	1.0752	1.0752	0
100	1.3069	1.3069	0
120	1.528	1.528	0
140	1.739	1.739	0
160	1.942	1.942	0
180	2.139	2.139	0
200	2.331	2.331	0
220	2.518	2.518	0
240	2.702	2.702	0
260	2.885	2.885	0
280	3.068	3.068	0
300	3.255	3.255	0
320	3.449	3.449	0
340	3.661	3.660	-0.001
360	3.916	3.916	0
370	4.114	4.113	-0.001
372	4.181	4.180	-0.001
374	4.326	4.318	-0.008
374.15	4.406	4.412	0.006

Table 26

Vapour enthalpy correlations

number of coefficients	k	maximum positive deviation J/g	corresponding temperature °C	maximum negative deviation J/g	corresponding temperature °C	maximum percentage deviation %	corresponding temperature °C	standard deviation J/g
12	.5	.831	373	-.921	374	.043	374	.180
12	.4	.399	321	-.345	301	.015	321	.131
12	.3	.444	321	-.360	373	.016	321	.139
12	.2	.395	321	-.359	301	.015	321	.135
12	.1	.412	321	-.383	301	.015	321	.141

Table 27

Comparison of vapour enthalpy equation with 1963 IST

temperature °C	vapour enthalpy, J/g		
	IST	Equation (143)	Δh/Tolerance
0	2501	2501	0/3
0.01	2501	2501	0/3
10	2519	2519	0/3
20	2538	2538	0/2
30	2556	2556	0/2
40	2574	2574	0/2
50	2592	2592	0/2
60	2609	2609	0/2
70	2626	2626	0/2
80	2643	2643	0/2
90	2660	2660	0/2
100	2676	2676	0/2
110	2691	2691	0/2
120	2706	2706	0/2
130	2720	2721	-1/2
140	2734	2734	0/2
150	2747	2747	0/3
160	2758	2758	0/3
170	2769	2769	0/3
180	2778	2778	0/4
190	2786	2786	0/4
200	2793	2793	0/4
210	2798	2798	0/4
220	2802	2802	0/4
230	2803	2803	0/4
240	2803	2803	0/4
250	2801	2801	0/4
260	2796	2796	0/4
270	2790	2789	1/4
280	2780	2779	1/4
290	2766	2766	0/4
300	2749	2749	0/4
310	2727	2727	0/5
320	2700	2700	0/6
330	2666	2666	0/6
340	2623	2622	1/7
350	2565	2564	1/8
360	2481	2481	0/8
370	2331	2331	0/12
371	2305	2305	0/14
372	2273	2272	1/16
373	2230	2229	1/18
374	2146	2147	-1/30
374.15	2095	2088	7/30

Table 20

Comparison of vapour volume from saturation equations with 1963 IST

temperature	vapour volume, cm^3/g		
°C	IST	saturation equations	Δv/Tolerance
0	206288	206328	-40/210
0.01	206146	206185	-39/210
10	106422	106420	2/110
20	57836	57838	-2/58
30	32929	32931	-2/33
40	19546	19547	-1/19
50	12045	12045	0/12
60	7677.4	7677.6	
70	5045.3	5045.3	0/50
80	3408.3	3408.4	-1/34
90	2360.9	2361.0	-1/24
100	1673.0	1673.0	0/17
110	1210.1	1210.1	0/12
120	891.71	891.74	-3/89
130	668.36	668.36	-4/67
140	508.68	508.69	-1/51
150	392.57	392.60	-3/39
160	306.85	306.86	-1/31
170	242.62	242.62	0/24
180	193.85	193.85	0/19
190	156.35	156.35	0/16
200	127.19	127.19	0/13
210	104.265	104.264	1/104
220	86.065	86.065	-3/86
230	71.472	71.478	-6/71
240	59.674	59.682	-8/60
250	50.056	50.062	-6/50
260	42.149	42.153	-4/42
270	35.599	35.601	-2/36
280	30.133	30.132	1/30
290	25.537	25.534	3/30
300	21.643	21.639	4/35
310	18.316	18.315	1/35
320	15.451	15.456	-5/35
330	12.967	12.970	-3/35
340	10.779	10.779	0/35
350	8.805	8.804	1/35
360	6.943	6.943	0/40
370	4.93	4.94	-1/10
371	4.68	4.69	-1/10
372	4.40	4.41	-1/11
373	4.05	4.07	-2/12
374	3.47	3.50	-3/12
374.15	3.17	3.15	2/15

Table 29

Comparison of vapour entropy from saturation equations and NEL Tables

temperature	s_g, J/g K		Δs_g
°C	NEL Tables	saturation equations	J/g K
0	9.155	9.155	0
20	8.666	8.666	0
40	8.256	8.256	0
60	7.909	7.909	0
80	7.611	7.611	0
100	7.355	7.355	0
120	7.130	7.130	0
140	6.930	6.931	0.001
160	6.751	6.751	0
180	6.586	6.586	0
200	6.431	6.432	0.001
220	6.285	6.285	0
240	6.142	6.143	0.001
260	6.001	6.001	0
280	5.857	5.857	0
300	5.705	5.705	0
320	5.535	5.536	0.001
340	5.336	5.336	0
360	5.053	5.053	0
370	4.795	4.795	0
372	4.702	4.701	-0.001
374	4.503	4.504	0.001
374.15	4.406	4.412	0.006

Table 30

Critical point values

Investigator	Year	t_c	p_c	v_c	Reference
Traube & Teichner	1904	374	-	-	(76)
Holborn & Baumann	1910	374.07	220.9	-	(77)
Schroer	1927	374.2	-	-	(78)
Keyes & Smith	1931	374.11	221.43	3.085	(79)
Keyes, Smith & Gerry	1934	374.11	221.061	-	(20)
Reichenfield & Chang	1935	374.20	-	3.04	(80)
Eck	1937	374.2	221.15	3.063	(81)
Osborne, Stimson & Ginnings	1937	374.15	221.28	3.1	(82)
Timrot	1952	374.15	221.29	3.3	(83)
Nowak & Grosh	1959	374.15	221.18	3.28	(84)
IST	1963	374.15 $\pm$0.10	221.02 $\pm$0.1	3.17 $\pm$0.15	-
Rivkin	1964	-	-	3.165 $\pm$0.019	(85)
Bridgeman & Aldrich	1965	374.02	222.261	3.1547	(75)
Juza	1966	374.07	221.06	3.16	(45)
Present work	1967	374.15	221.23	3.15	-
Blank	1968	373.91 $\pm$0.03	220.45 $\pm$0.03	-	(86)

Table 31

Comparison of correlated and experimental vapour pressure values at the critical point

temperature °C	pressure, bar BA	1966 K function	1967 K function	equation (137)	Measured Value	Investigator
373.91	220.62	220.57	220.57	220.60	220.45	Blank
374.02	220.91	220.86	220.86	220.89	220.61	BA
374.07	221.04	220.99	220.99	221.02	221.06	Juza
374.11	221.15	221.09	221.09	221.13	221.06	Smith & Keyes
374.15	221.25_6	221.20	221.20	221.23	221.2	OSG & IST

Table 32

Comparison of vapour pressure derivatives above 370 °C

Temp. °C	$T\frac{dp}{dT}$, J/cm³								
	NBS 1932	Egerton and Callendar	Keyes (M.I.T.)	NBS 1939	Bridgeman and Aldrich	1966 K function	Equation (137)	Averages with K	Averages without K
370	161.91	162.40	161.48	161.94	161.97	164.22	161.83	162.25	161.92
372	166.31	166.82	165.69	166.60	166.57	168.63	166.25	166.69	166.37
374	170.93	171.41	170.08	172.53	171.57	173.27	170.91	171.52	171.24
374.15	"	"	"	173.13	171.91	173.63	171.27	172.48	172.10

Table 33

Critical point derivatives

Property Y	Derivative $\left(\frac{dY}{dT}\right)_c$	
	Theoretical	Saturation equations
p	finite	0.26459 J/cm^3 K
v_f, h_f, s_f, β'	∞	∞
v_g, h_g, s_g, γ	$-\infty$	$-\infty$
α	finite	4.0302 J/g K

Table 34

Evaluation of the thermodynamic consistency for the saturation equations

emperature	specific free enthalpy, J/g		derivative, J/cm^3	
^oC	$g_f = g_g$	$g_f - g_g$	$T\frac{dp}{dT}$	$T\frac{dp}{dT} - T\frac{s_{fg}}{v_{fg}}$
0	.001	$-7.60_{10}-9$	.01212	$-2.84_{10}-14$
20	-2.998	$-7.92_{10}-9$	.04242	0
40	-11.709	$6.05_{10}-9$	.12311	$-6.82_{10}-13$
60	-25.753	$1.40_{10}-9$	.30715	0
80	-44.810	$-7.45_{10}-9$	.67741	0
100	-68.594	$-4.66_{10}-9$	1.3498	$3.64_{10}-12$
120	-96.853	$2.79_{10}-9$	2.4729	0
140	-129.36	$-3.73_{10}-9$	4.2255	0
160	-165.90	$-1.86_{10}-9$	6.8115	0
180	-206.30	$-1.86_{10}-9$	10.455	0
200	-250.38	$-3.73_{10}-9$	15.396	0
220	-297.97	0	21.889	$-1.16_{10}-10$
240	-348.93	0	30.206	0
260	-403.11	$3.73_{10}-9$	40.648	$-1.16_{10}-10$
280	-460.39	$3.73_{10}-9$	53.565	$-1.16_{10}-10$
300	-520.64	$7.45_{10}-9$	69.389	$-2.33_{10}-10$
320	-583.74	$3.73_{10}-9$	88.694	0
340	-649.60	$7.45_{10}-9$	112.38	$-6.98_{10}-10$
360	-718.11	0	142.52	$4.66_{10}-10$
370	-753.33	$3.73_{10}-9$	161.83	$-1.40_{10}-9$
372	-760.45	0	166.25	0
374	-767.59	$3.73_{10}-9$	170.91	$-3.73_{10}-9$
374.15	-768.13	0	171.27	$-5.04_{10}-7$

Table 35

Derivation of thermodynamic properties for equations in different variables

given function / other properties	$h(s,p)$	$f(v,t)$	$p(v,T)$
p	p	$-\frac{\partial f}{\partial v}$	p
T	$\frac{\partial h}{\partial s}$	T	T
v	$\frac{\partial h}{\partial p}$	v	v
s	s	$-\frac{\partial f}{\partial T}$	$-\int_{v_o}^{v}\frac{\partial p}{\partial T}\,dv$
h	h	$f-T\frac{\partial f}{\partial T}-v\frac{\partial f}{\partial v}$	$-\int_{v_o}^{v}p\,dv-T\int_{v_o}^{v}\frac{\partial p}{\partial T}\,dv+pv$
c_p	$\frac{\frac{\partial h}{\partial s}}{\frac{\partial^2 h}{\partial s^2}}$	$-\frac{T\{\frac{\partial^2 f}{\partial v^2}\cdot\frac{\partial^2 f}{\partial T^2}-\frac{\partial^2 f}{\partial v\partial T}\}}{\frac{\partial^2 f}{\partial v^2}}$	$\frac{-T\{\frac{\partial p}{\partial v}\left[\int_{v_o}^{v}\frac{\partial^2 p}{\partial T^2}\,dv\right]+\{\frac{\partial p}{\partial T}\}^2\}}{\frac{\partial p}{\partial v}}$
f	$h-p\frac{\partial h}{\partial p}-s\frac{\partial h}{\partial s}$	f	$-\int_{v_o}^{v}p\,dv$

Table 36

Correlations for different isobars using NEL Tables as input data

pressure bar	maximum positive deviation J/g	corresponding entropy J/g K	maximum negative deviation J/g	corresponding entropy J/g K	maximum percentage deviation %	corresponding entropy J/g K	standard deviation enthalpy J/g	standard deviation temperature deg C
1000	0.70	5.936	-0.83	4.204	0.060	0.270	0.307	0.486
900	0.71	5.746	-0.81	3.190	-0.065	0.536	0.329	0.513
800	1.00	3.367	-0.72	5.671	0.066	3.367	0.324	0.521
700	0.75	3.720	-0.69	3.076	0.077	0.672	0.306	0.4-0
600	0.96	5.648	-0.85	3.179	-0.131	-0.001	0.325	0.548
500	0.84	5.953	-0.82	5.993	0.124	0.145	0.311	0.512
400	0.77	6.522	-0.88	6.634	-0.174	0.001	0.321	0.537
300	0.74	6.698	-1.21	6.234	-1.307	0.001	0.393	0.562
250	1.53	3.575	-1.73	4.176	-2.049	0.001	0.513	0.634

Table 37

Evaluation of equation for p = 700 bar

entropy J/g K	h_{EQN}	enthalpy h_{NEL}	J/g Δh	temperature °C	Δt
-0.002	68.4	68.4	-0.01	0	2.24
0.672	268.9	268.7	-0.21	50	-0.09
1.257	472.6	472.2	-0.02	100	0.01
1.772	677.0	677.2	0.17	150	0.02
2.239	886.1	886.3	0.18	200	0.04
2.671	1101.2	1101	-0.24	250	-0.29
3.076	1323.3	1324	0.69	300	-0.38
3.473	1560.9	1561	0.06	350	-0.41
3.886	1829.0	1829	0.01	400	-0.89
4.312	2126.6	2127	0.39	450	0.50
4.769	2468.3	2468	-0.30	500	0.27
5.176	2792.7	2793	0.27	550	0.05
5.494	3062.1	3062	-0.09	600	0.03
5.746	3288.2	3288	-0.23	650	-0.31
5.955	3486.3	3486	-0.35	700	-0.52
6.137	3668.0	3668	0.00	750	-0.22
6.300	3838.7	3839	0.31	800	1.78

Table 38

Effects of constraints on the equation for p = 700 bar

Constraints	Number of Coefficients	Standard deviations		Maximum	corresponding		
		h	t	Δt	t	Δt_o	Δt_{800}
NONE	10	0.306	0.490	1.07	790	-2.24	-1.78
h_o	11	0.306	0.484	1.06	790	-2.15	-1.77
h_o, T_o	12	0.309	0.382	1.00	390	0	-1.10
h_o, h_{800}	12	0.311	0.526	1.25	780	-1.70	0.88
h_o,T_o,h_{800},T_{800}	14	0.314	0.465	1.07	720	0	0

Table 39

Effects of derivatives on the equation for p = 700 bar

λ	standard deviation		Maximum Δt, deg. C				
	h, J/g	t, °C	0°C	390°C	720°C	790°C	800°C
0	0.306	0.490	-2.235	0.984	0.657	-1.069	-1.775
10^{-5}	0.308	0.491	-2.186	0.977	0.671	-0.998	-1.703
10^{-4}	0.310	0.502	-2.120	0.940	0.872	-0.836	-1.536
10^{-3}	0.549	1.174	-1.726	0.586	2.789	1.300	0.631

Table 40

High pressure correlations

		1000 bar			900 bar			800 bar			700 bar		
n	m	h	t	v	h	t	v	h	t	v	h	t	v
9	1	1.09	1.10	0.203	0.53	0.52	0.087	0.72	0.55	0.081	1.43	1.09	0.331
9	2	0.31	0.49	0.025	0.35	0.44	0.006	0.36	0.34	0.008	0.32	0.57	0.040
9	3	0.31	0.46	0.015	0.35	0.50	0.004	0.36	0.32	0.007	0.31	0.39	0.041
9	4	0.31	0.45	0.048	0.35	0.49	0.010	0.36	0.33	0.006	0.31	0.66	0.037
9	5	0.31	0.42	0.050	0.34	0.47	0.010	0.35	0.33	0.007	0.31	0.63	0.066
9	6	0.31	0.43	0.098	0.34	0.50	0.013	0.35	0.33	0.014	0.31	0.52	0.074
6	3	0.35	1.08	0.014	0.41	1.32	0.006	0.42	1.55	0.007	0.47	2.03	0.016
7	3	0.32	0.80	0.015	0.34	1.07	0.009	0.36	1.49	0.014	0.42	2.29	0.018
8	3	0.31	0.47	0.015	0.35	0.68	0.005	0.35	0.84	0.010	0.34	1.22	0.022
9	3	0.31	0.46	0.015	0.35	0.50	0.004	0.36	0.32	0.007	0.31	0.39	0.041
10	3	0.31	1.03	0.022	0.35	0.47	0.007	0.36	0.39	0.005	0.31	0.38	0.027
11	3	0.31	2.14	0.048	0.33	0.94	0.011	0.37	1.31	0.018	0.31	0.77	0.040

Table 41

Comparison of equation with 1963 IST

p bar	max Δh	h J/g	Tol.	max Δt	t °C	%Δt	max Δv	v cm^3/g	Tol.
1000	-0.87	2102	8	1.48	0	0.54	0.030	1.513	0.003
900	-0.97	1416	2	2.04	800	0.19	0.019	4.841	0.02
800	0.89	1508	2	1.02	390	0.15	0.037	5.484	0.02
700	0.74	3805	14	-1.92	0	-0.70	-0.187	6.326	0.02

Table 42

Correlations for different isobars based on Whalley's data

pressure bar	Number of coeff-icients	Maximum positive deviation J/g	entropy J/g K	Maximum negative deviation J/g	entropy J/g K	Maximum percentage deviation %	entropy J/g K	standard deviation enthalpy J/g	standard deviation temperature deg. C
1000	5	0.0031	0.2425	-0.0046	-0.0081	-0.0048	-0.0081	0.0014	0.020
800	5	0.0033	1.2335	-0.0131	-0.0046	-0.0169	-0.0046	0.0017	0.017
700	5	0.0031	1.1345	-0.0066	-0.0031	-0.0097	-0.0031	0.0014	0.016
600	5	0.0032	1.1408	-0.0106	-0.0019	-0.0181	-0.0019	0.0016	0.016
500	5	0.0030	1.1472	-0.0024	-0.0009	-0.0048	-0.0009	0.0013	0.016

Table 43

Evaluation of equation for p = 1000 bar

entropy J/g K	enthalpy J/g	Δh J/g	temperature °C	Δt deg C
-0.008	95.5	0.005	0	0.098
0.337	194.0	-0.001	25	-0.025
0.658	293.8	0.001	50	-0.010
0.958	394.2	0.000	75	-0.009
1.237	495.0	0.001	100	-0.022
1.500	596.2	0.001	125	-0.008
1.747	697.8	-0.002	150	-0.009

Table 44

Compressed water correlations

n	m	standard deviation				maximum deviation				maximum percentage deviations			
		h J/g	t deg C	v cm^3/g	c_p J/g K	h J/g	t deg C	v cm^3/g	c_p J/g K	h %	t %	v %	c_p %
4	2	0.0043	0.0182	0.00066	0.0056	0.0222	0.1452	0.00197	0.0379	0.733	0.034	0.191	0.918
4	3	0.0012	0.0178	0.00015	0.0056	0.0087	0.1104	0.00095	0.0370	0.259	0.026	0.087	0.879
4	4	0.0015	0.0205	0.00030	0.0063	0.0137	0.1731	0.00139	0.0471	0.286	0.041	0.251	1.157

Table 45

Comparison of values derived from equation (155) with

1963 IST values and tolerances

COMPRESSED WATER

	Volume cm^3/g				Enthalpy J/g			
t^oC	0	50	100	150	0	50	100	150
p bar								
1(a)	1.00012	1.0121			0.059	209.38		
(b)	1.0002	1.0121			0.06	209.3		
(c)	-0.8	0			-0.1	0.8		
(d)	1	2			1	1		
5	0.9999	1.0119	1.0432	1.0905	0.465	209.7	419.4	632.0
	0.9999	1.0119	1.0433	1.0906	0.47	209.6	419.4	632.2
	0	0	-1	-1	-0.5	1	0	-2
	2	2	2	3	2	2	2	3
10	0.9996	1.0117	1.0430	1.0901	0.97	210.2	419.8	632.3
	0.9997	1.0117	1.0431	1.0903	0.98	210.1	419.7	632.4
	-1	0	-1	-2	-1	1	1	-1
	2	2	2	3	2	2	4	4
25	0.9989	1.0110	1.0422	1.0891	2.49	211.4	420.9	633.2
	0.9989	1.0110	1.0423	1.0894	2.50	211.3	421.0	633.4
	0	0	-1	-3	-1	1	-1	-2
	2	2	2	3	5	2	4	4
50	0.9976	1.0099	1.0410	1.0875	5.02	213.6	422.8	634.8
	0.9976	1.0099	1.0410	1.0878	5.05	213.5	422.8	634.9
	0	0	0	-3	-3	1	0	-1
	2	2	2	3	10	2	4	4
75	0.9964	1.0088	1.0397	1.0859	7.53	215.7	424.7	636.3
	0.9964	1.0088	1.0398	1.0862	7.58	215.7	424.7	636.5
	0	0	-1	-3	-5	0	0	-2
	2	2	3	4	15	2	4	4
100	0.9951	1.0077	1.0385	1.0842	10.0	217.9	426.6	637.9
	0.952	1.0077	1.0386	1.0846	10.1	217.9	426.6	638.1
	-1	0	4	-4	-1	0	0	-2
	2	2	4	4	2	2	4	4
125	0.9939	1.0067	1.0373	1.0826	12.5	220.0	428.4	639.5
	0.9940	1.0066	1.0373	1.0830	12.6	220.0	428.5	639.7
	-1	1	0	-4	-1	0	-1	-2
	2	2	4	4	3	2	4	4
150	0.9927	1.0056	1.0361	1.0811	15.0	222.2	430.3	641.1
	0.9928	1.0055	1.0361	1.0813	15.1	222.1	430.4	641.3
	-1	1	0	-2	-1	1	-1	-2
	2	2	4	4	3	2	4	4
175	0.9915	1.0045	1.0349	1.0795	17.5	224.3	432.2	642.7
	0.9915	1.0044	1.0348	1.0798	17.6	224.3	432.3	642.9
	0	1	1	-3	-1	0	-1	-2
	2	2	4	4	4	3	4	4

Table 45 continued .....

	Volume cm^3/g				Enthalpy J/g			
t °C								
p bar	0	50	100	150	0	50	100	150
200	0.9903	1.0035	1.0337	1.0780	20.0	226.5	434.1	644.2
	0.9904	1.0033	1.0336	1.0782	20.1	226.5	434.2	644.5
	-1	2	1	-2	-1	0	-1	-3
	2	2	4	4	4	3	4	4
225	0.9891	1.0024	1.0325	1.0764	22.4	228.6	436.0	645.8
	0.9892	1.0023	1.0324	1.0766	22.6	228.6	436.1	646.1
	-1	1	1	-2	-2	0	-1	-3
	2	2	4	4	5	3	4	4
250	0.9879	1.0014	1.0313	1.0749	24.9	230.7	437.9	647.5
	0.9880	1.0012	1.0313	1.0751	25.1	230.7	438.0	647.7
	-1	2	0	-2	-2	0	-1	-2
	2	2	4	4	5	3	4	4
275	0.9868	1.0004	1.0301	1.0734	27.3	232.9	439.8	649.1
	0.9868	1.0002	1.0301	1.0736	27.5	232.8	439.8	649.3
	0	2	0	-2	-2	1	-1	-2
	2	2	4	4	5	3	4	4
300	0.9856	0.9993	1.0290	1.0720	29.8	235.0	441.7	650.7
	0.9856	0.9992	1.0289	1.0721	30.0	235.0	441.8	650.9
	0	1	1	-1	-2	0	-1	-2
	2	2	4	4	5	3	4	4
350	0.9833	0.9973	1.0267	1.0690	34.6	239.3	445.5	653.9
	0.9834	0.9972	1.0267	1.0692	34.9	239.2	445.6	654.1
	-1	1	0	-2	-3	1	-1	-2
	2	2	4	4	6	3	4	4
400	0.9810	0.9953	1.0245	1.0662	39.4	243.5	449.3	657.2
	0.9811	0.9951	1.0244	1.0664	39.7	243.5	449.4	657.4
	-1	2	1	-2	-3	0	-1	-2
	2	2	4	4	7	3	4	4
450	0.9788	0.9933	1.0222	1.0634	44.2	247.8	453.1	660.5
	0.9788	0.9932	1.0222	1.0636	44.6	247.7	453.2	660.7
	0	1	0	-2	-4	1	-1	-2
	2	2	4	4	8	4	4	4
500	0.9766	0.9913	1.0201	1.0607	49.0	252.0	256.9	663.8
	0.9766	0.9912	1.0200	1.0609	49.3	252.0	457.0	664.0
	0	1	1	-2	-3	0	-1	-2
	2	3	4	5	8	4	4	4
550	0.9745	0.9894	1.0179	1.0580	53.7	256.2	460.7	667.2
	0.9745	0.9892	1.0178	1.0582	54.1	256.2	460.8	667.3
	0	2	1	-2	-4	0	-1	-1
	3	3	4	5	8	4	4	4
600	0.9723	0.9875	1.0158	1.0554	58.4	260.4	464.5	670.5
	0.9723	0.9873	1.0157	1.0556	58.8	260.4	464.6	670.6
	0	2	1	-2	-4	0	-1	-1
	3	3	4	5	9	4	4	4
650	0.9703	0.9856	1.0138	1.0528	63.1	264.6	468.3	673.9
	0.9703	0.9854	1.0137	1.0530	63.5	264.6	468.4	674.0
	0	2	1	-2	-4	0	-1	-1
	3	3	4	5	10	4	4	5

Table 45 continued.....

t°C / p bar	Volume cm^3/g 0	50	100	150	Enthalpy J/g. 0	50	100	150
700	0.9682	0.9838	1.0117	1.0503	67.7	268.8	472.1	677.3
	0.9682	0.9836	1.0116	1.0505	68.1	268.8	472.1	677.3
	0	2	1	-2	-4	0	0	0
750	0.9662	0.9820	1.0097	1.0479	72.4	273.0	476.0	680.7
	0.9662	0.9818	1.0096	1.0480	72.7	273.0	476.0	680.7
	0	2	1	-1	-3	0	0	0
	3	3	4	5	11	6	5	5
800	0.9642	0.9802	1.0078	1.0455	77.0	277.2	479.8	684.1
	0.9642	0.9800	1.0076	1.0456	77.3	277.1	470.8	684.0
	0	2	2	-1	-3	1	0	1
	3	3	4	5	12	7	7	7
850	0.9622	0.9784	1.0058	1.0432	81.5	281.4	483.6	687.5
	0.9622	0.9782	1.0057	0.0432	81.9	281.3	483.6	687.4
	0	2	1	0	-4	1	0	1
	3	3	4	5	12	8	8	8
900	0.9603	0.9767	1.0039	1.0409	86.1	285.5	487.4	690.9
	0.9603	0.9765	1.0038	1.0409	86.5	285.4	487.3	690.8
	0	2	1	0	-4	1	1	1
	3	3	4	5	12	9	9	9
950	0.9584	0.9750	1.0021	1.0387	90.6	289.7	491.2	694.4
	0.9584	0.9748	1.0019	1.0386	91.1	289.6	491.2	694.2
	0	2	2	1	-5	1	0	2
	3	3	4	5	12	10	10	10
1000	0.9566	0.9733	1.0002	1.0365	95.1	293.9	495.1	697.8
	0.9566	0.9731	1.0000	1.0363	95.7	293.7	495.0	697.6
	0	2	2	2	-6	2	1	2
	3	3	4	5	12	12	12	12

(a) equation(155) value

(b) IST value

(c) equation value - IST value

(d) IST tolerance

Table 46

Comparison of saturated liquid values with

1963 IST values and tolerances

$t^{\circ}C$	p bar	v_f cm^3/g eqn(155)	v_f cm^3/g IST	Δv	Tol.	h_f J/g eqn(155)	h_f J/g IST	Δh	Tol.
0	0.006108	1.00013	1.00021	-8	5	-0.0415	-0.0416	1	4
.01	0.006112	1.00013	1.00021	-8	5	0.000611	0.000611	0	1
10	0.012271	1.00032	1.0004	-0.8	1	42.00	41.99	1	4
20	0.023368	1.0018	1.0018	0	1	83.91	83.86	5	8
30	0.042418	1.0044	1.0044	0	1	125.74	125.66	8	8
40	0.073750	1.0079	1.0079	0	1	167.52	167.47	5	8
50	0.12335	1.0121	1.0121	0	2	209.3	209.3	0	1
60	0.19919	1.0171	1.0171	0	2	251.1	251.1	0	1
70	0.31161	1.0227	1.0228	-1	2	293.0	293.0	0	1
80	0.47358	1.0290	1.0290	0	3	334.9	334.9	0	2
90	0.70109	1.0359	1.0359	0	3	377.0	376.9	1	2
100	1.01325	1.0434	1.0435	-1	3	419.1	419.1	0	2
110	1.4327	1.0515	1.0515	0	4	461.4	461.3	1	2
120	1.9854	1.0603	1.0603	0	4	503.8	503.7	1	2
130	2.7011	1.0697	1.0697	0	4	546.4	546.3	1	3
140	3.6136	1.0797	1.0798	-1	4	589.1	589.1	0	3
150	4.7597	1.0905	1.0906	-1	4	632.0	632.2	-2	3

Table 47

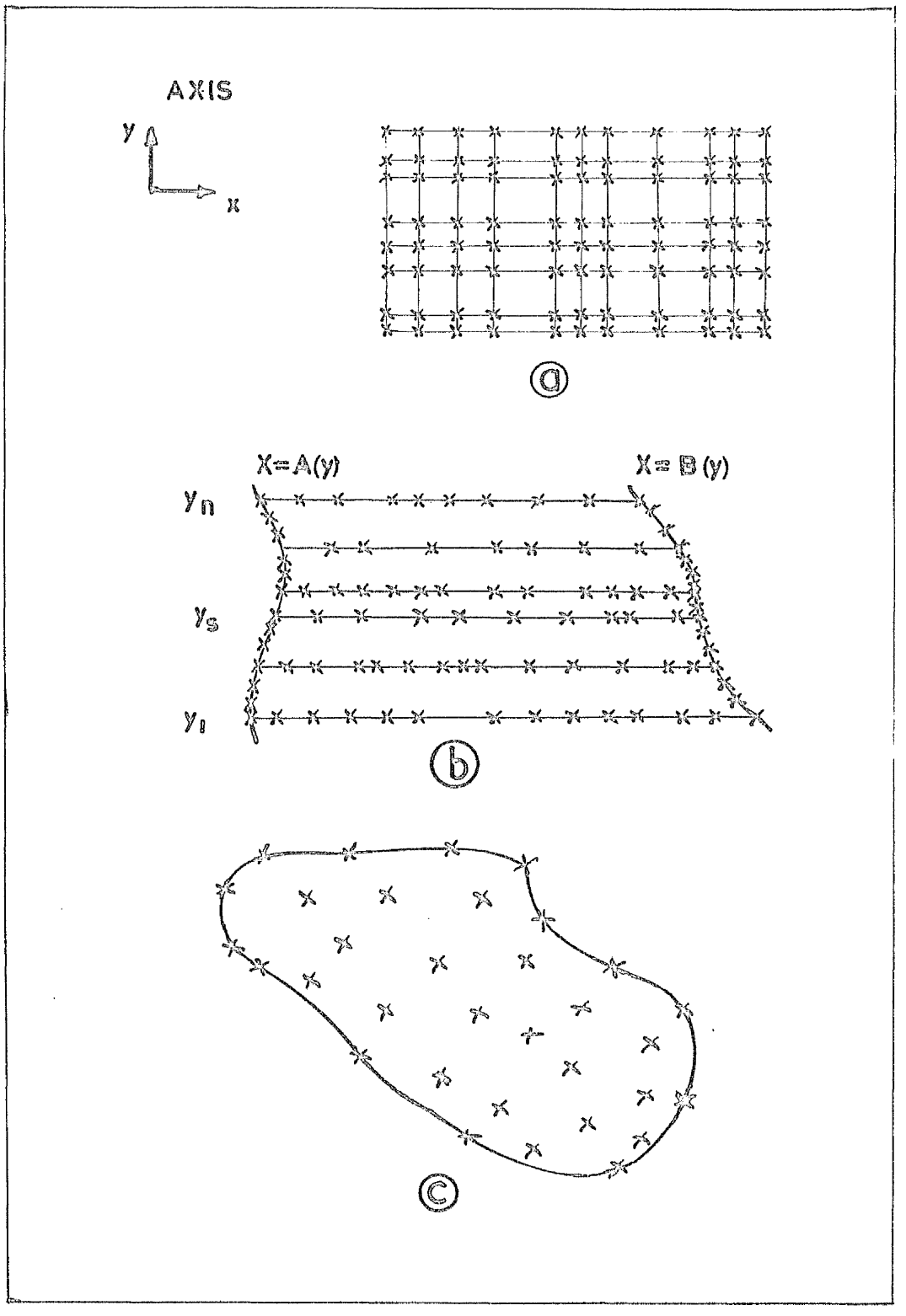
Comparison of saturated liquid values

°C	p bar	v_f cm^3/g App. IV	v_f cm^3/g eqn(155)	h_f J/g App.IV	h_f J/g eqn(155)	s_f J/g K App. IV	s_f J/g K eqn(155)	c_{p_f} J/gK eqn(156)	c_{p_f} J/gK eqn(155)
0	0.006107	1.00018	1.00013	-0.0416	-0.0415	-0.0002	-0.0001	4.218	4.214
01	0.006111	1.00018	1.00013	0.00631	0.000611	0.0000	0.0000	4.218	4.214
10	0.012277	1.00039	1.00032	42.00	42.00	0.1510	0.1511	4.193	4.197
20	0.023378	1.0018	1.0018	83.86	83.91	0.2963	0.2965	4.182	4.186
30	0.042433	1.0044	1.0044	125.66	125.74	0.4365	0.4368	4.179	4.180
40	0.073774	1.0078	1.0078	167.45	167.52	0.5721	0.5724	4.179	4.177
50	0.123383	1.0121	1.0121	209.25	209.30	0.7035	0.7037	4.181	4.179
60	0.19924	1.0171	1.0171	251.08	251.11	0.8310	0.8311	4.184	4.183
70	0.31166	1.0227	1.0227	292.96	292.98	0.9548	0.9549	4.190	4.189
80	0.47364	1.0290	1.0290	334.90	334.92	1.0753	1.0753	4.196	4.197
90	0.70112	1.0360	1.0359	376.93	376.96	1.1925	1.1926	4.205	4.207
00	1.01325	1.0435	1.0434	419.05	419.11	1.3069	1.3070	4.216	4.218
10	1.4326	1.0516	1.0515	461.30	461.38	1.4185	1.4187	4.229	4.231
20	1.9853	1.0603	1.0603	503.7	503.8	1.528	1.528	4.245	4.244
30	2.7011	1.0697	1.0697	546.3	546.4	1.634	1.635	4.263	4.259
40	3.6135	1.0798	1.0797	589.1	589.1	1.739	1.739	4.285	4.274
50	4.7597	1.0905	1.0905	632.1	632.0	1.842	1.841	4.310	4.289

Table 48

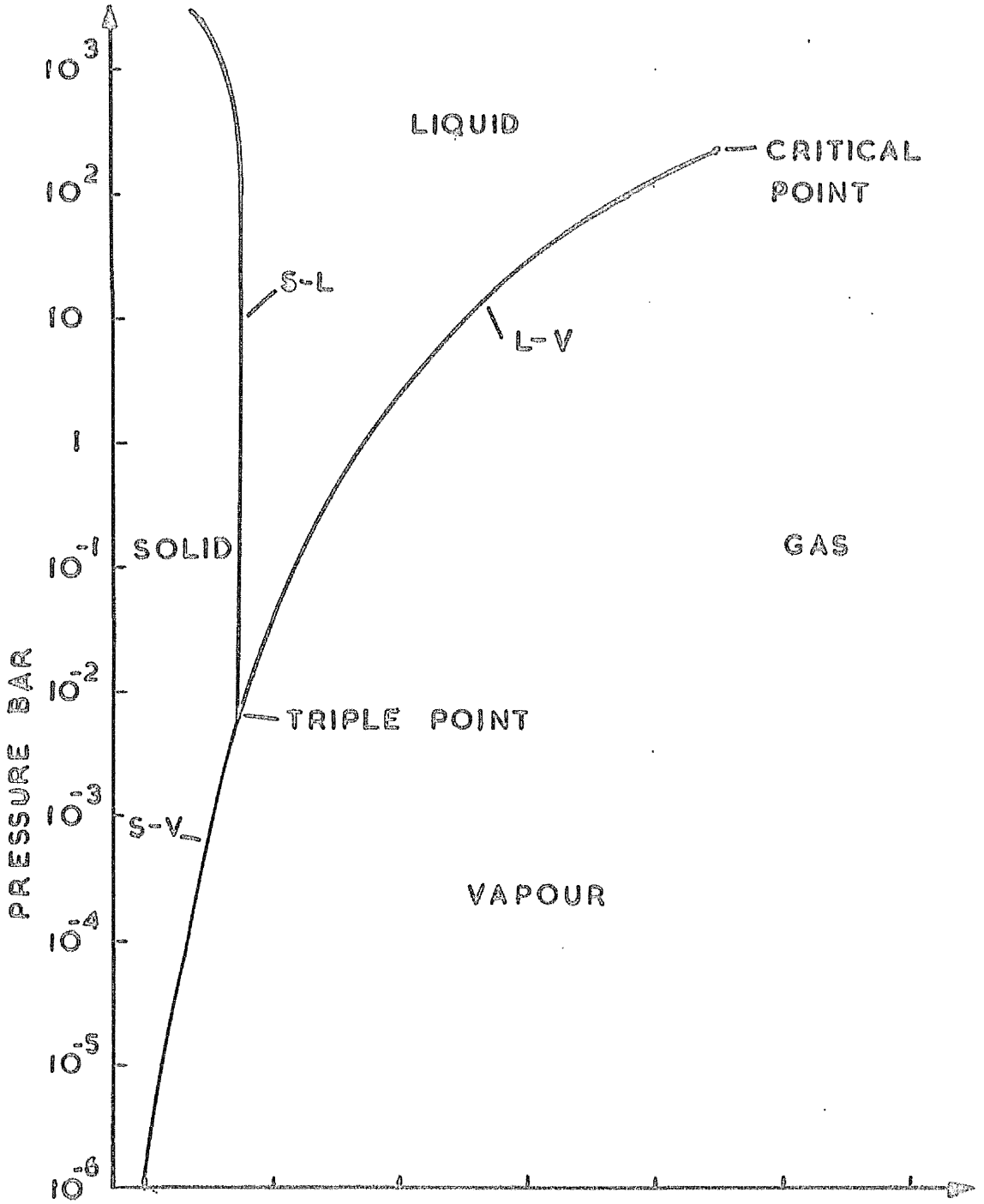
Conditions for characteristic curves

Curve	Condition
J	$Z = 1$
A	$\left(\frac{\partial Z}{\partial T}\right)_v = 0$ or $\frac{T}{p}\left(\frac{\partial p}{\partial T}\right)_v = 1$
B	$\left(\frac{\partial Z}{\partial p}\right)_T = \left(\frac{\partial Z}{\partial v}\right)_T = 0$ or $\frac{p}{v}\left(\frac{\partial v}{\partial p}\right)_T = -1$
C	$\left(\frac{\partial Z}{\partial T}\right)_p = 0$ or $\frac{T}{v}\left(\frac{\partial v}{\partial T}\right)_p = 1$
B_p	$\left(\frac{\partial\, v}{\partial T \partial p}\right) = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p \left(\frac{\partial v}{\partial p}\right)_T$
C_T	$\left(\frac{\partial^2 h}{\partial p^2}\right)_T = \frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T \left(\frac{\partial h}{\partial p}\right)_T$



ARRANGEMENT OF DATA IN SURFACE FITTING PROBLEM

fig. 1



p-T DIAGRAM FOR WATER SUBSTANCE

fig. 2

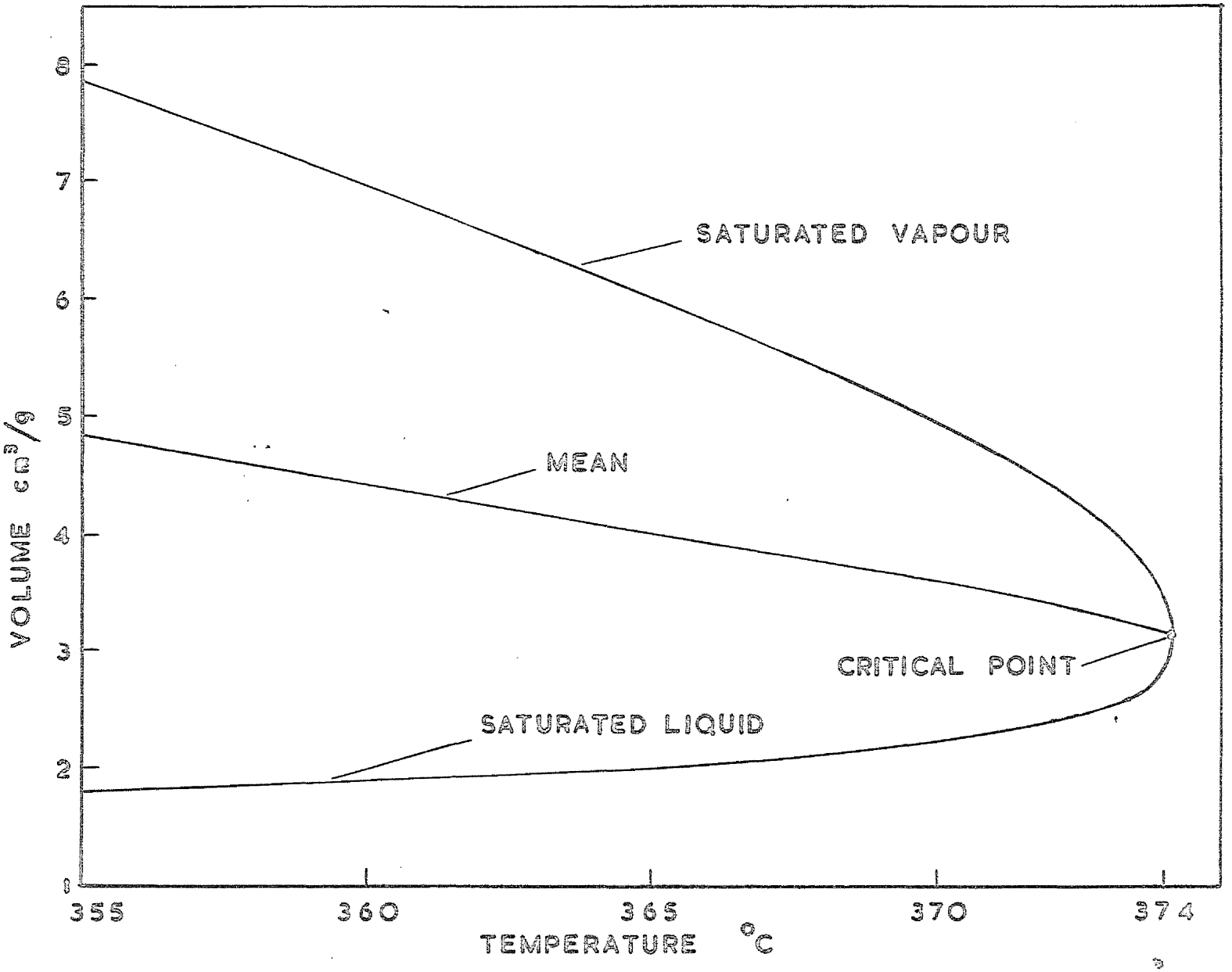
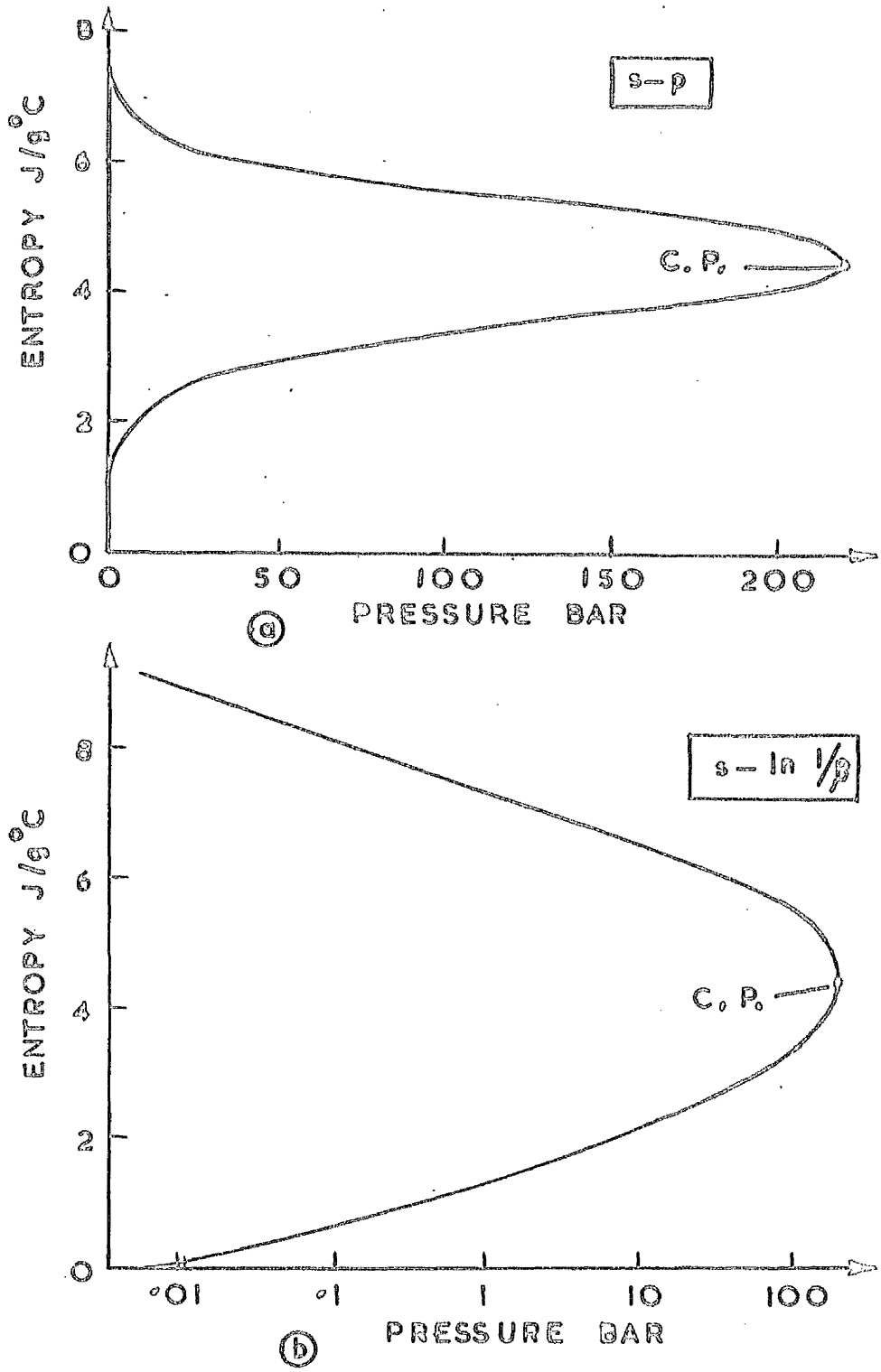
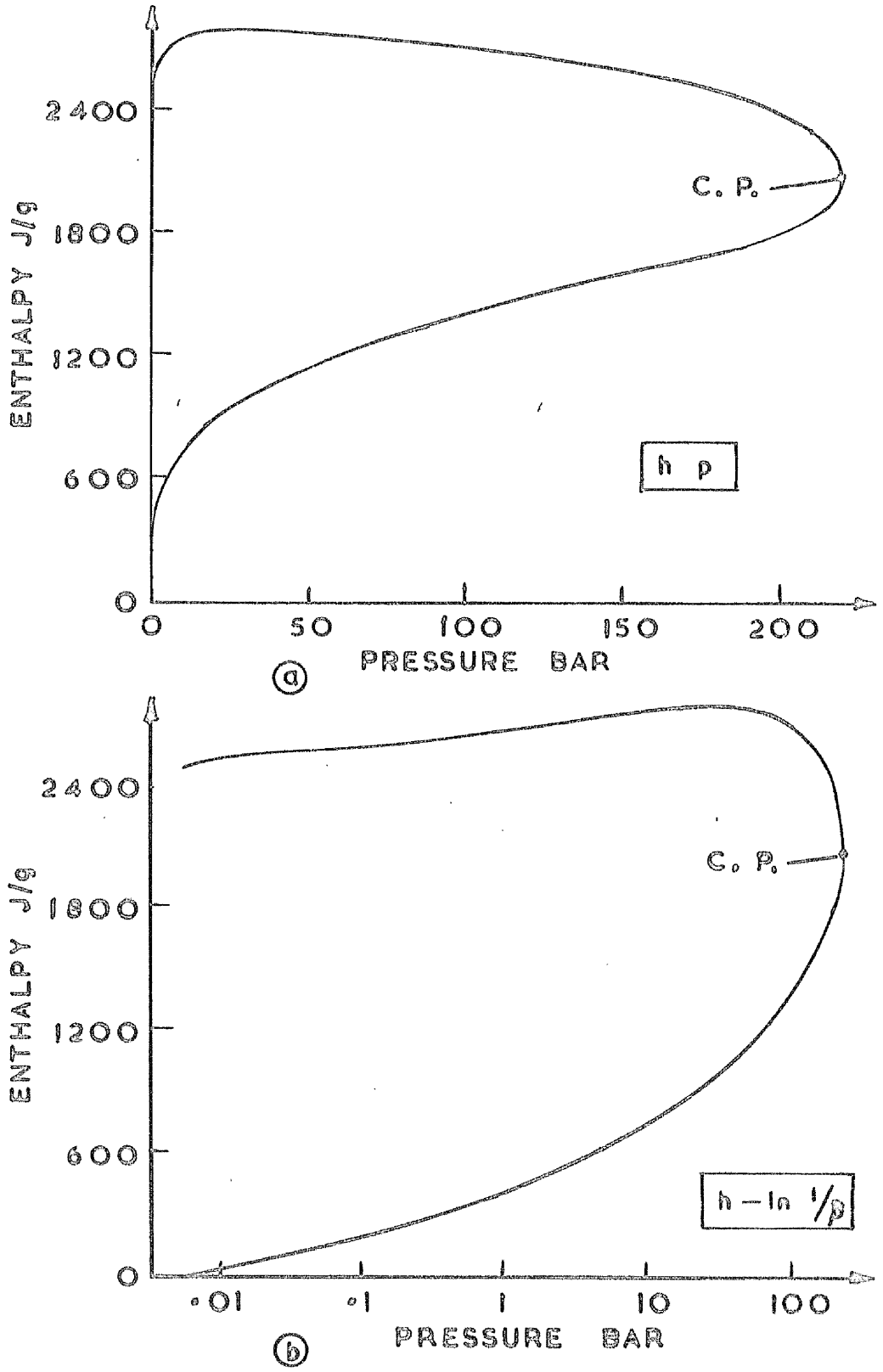


fig. 3 v-T DIAGRAM FOR THE SATURATION LINE



Δ AND p FOR THE SATURATION LINE

fig. 4



h AND p FOR THE SATURATION LINE

fig. 5

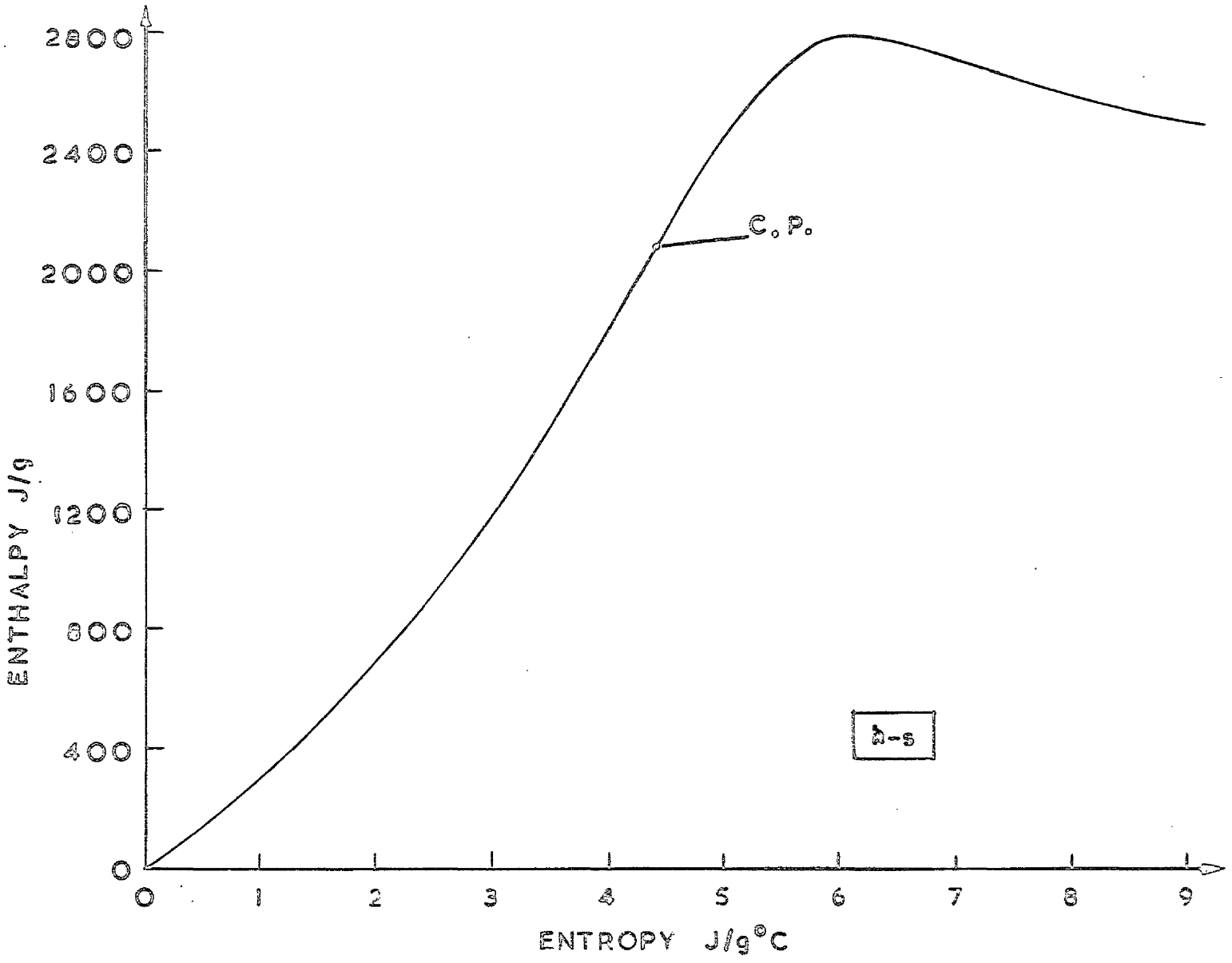
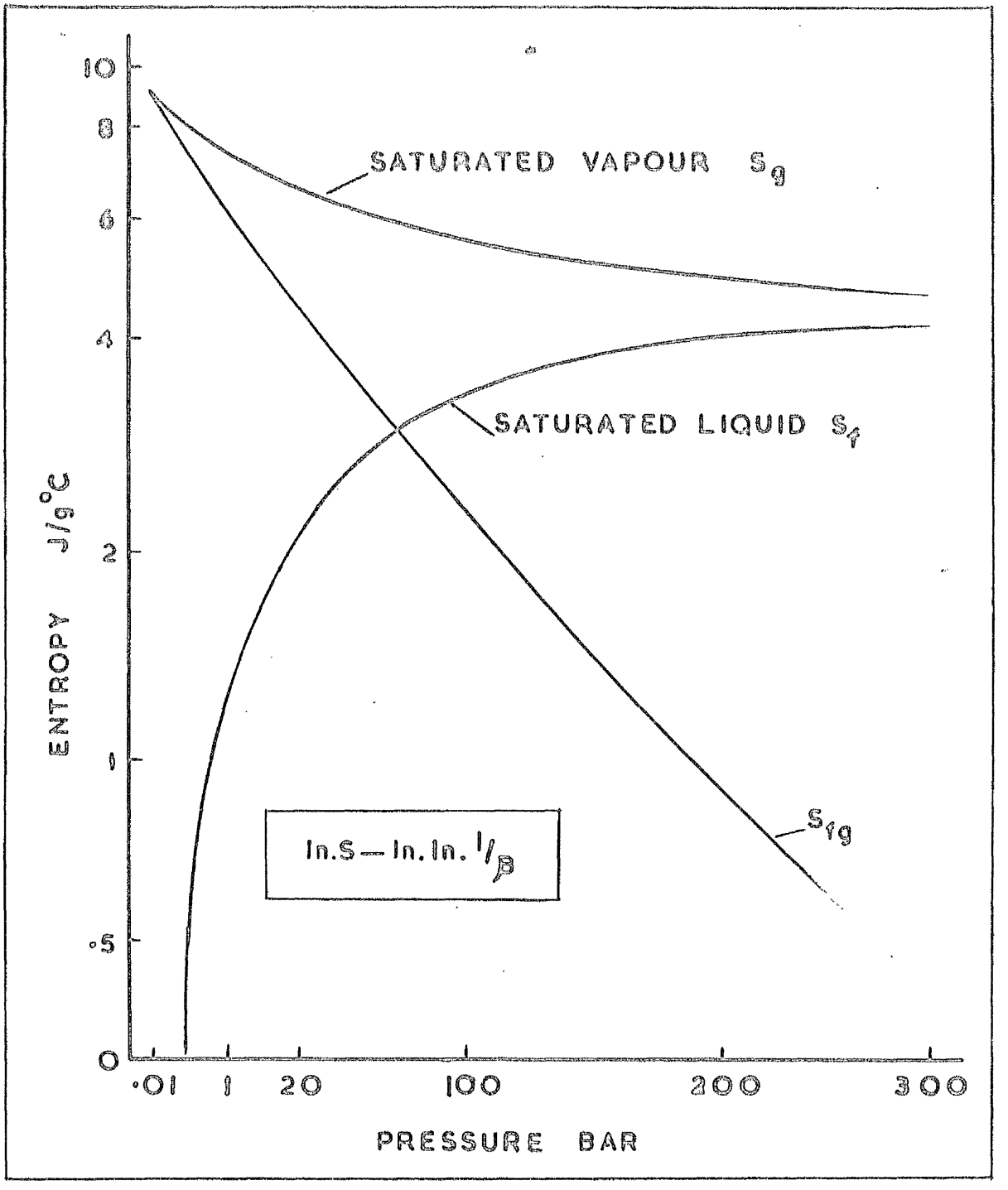
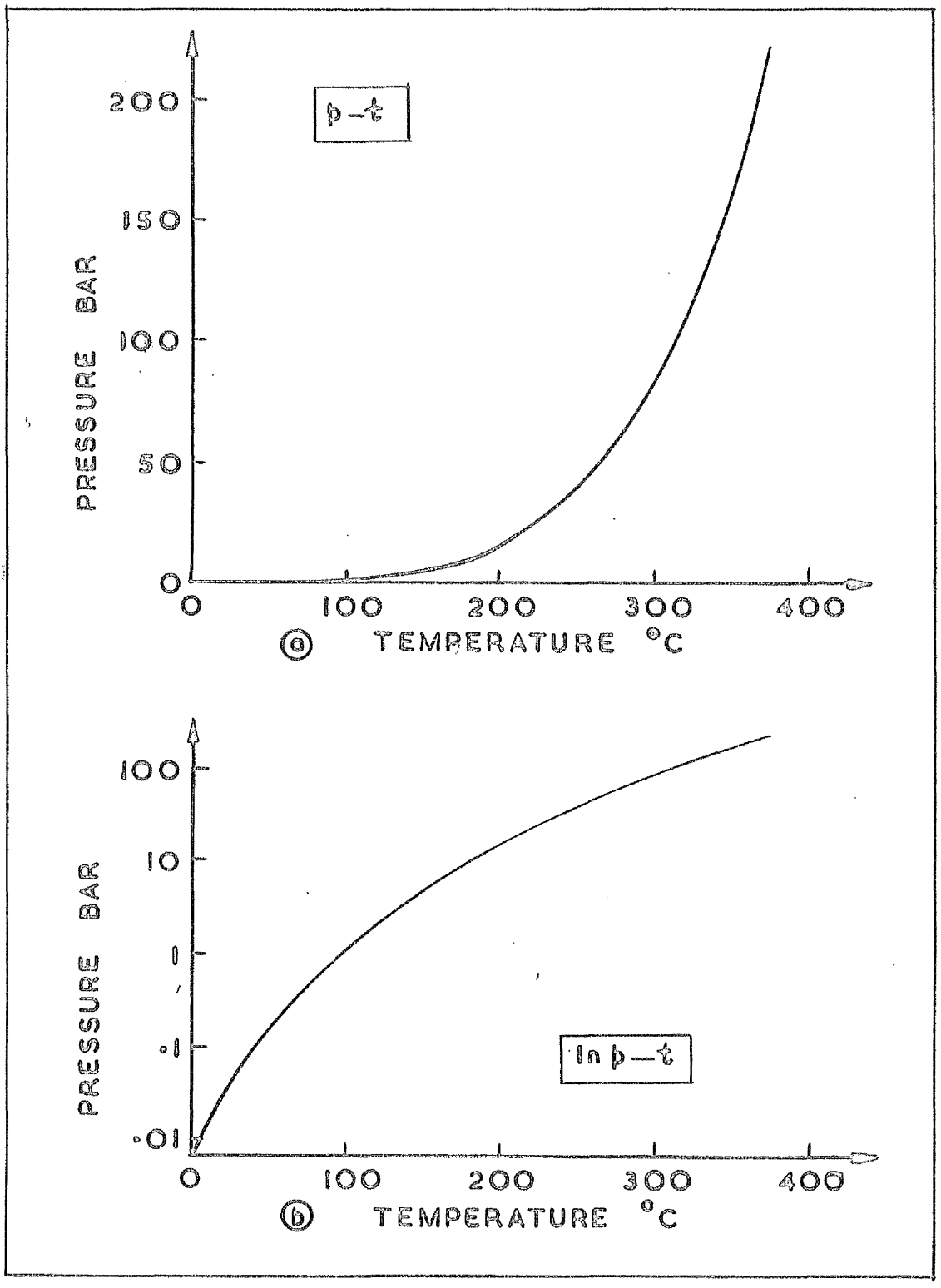


fig.6 $\mathcal{A}$ AND $\triangle$ FOR THE SATURATION LINE



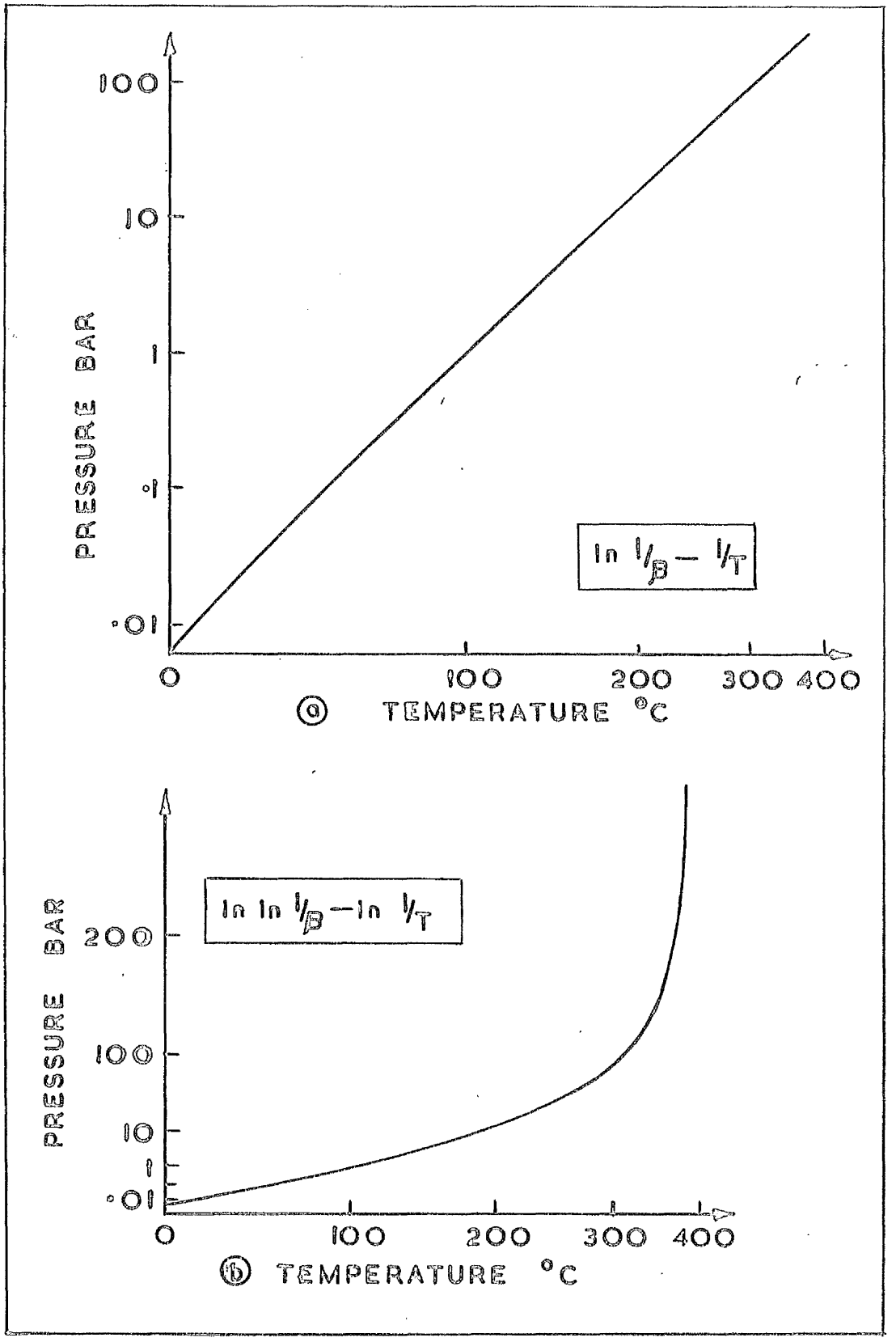
α AND β FOR THE SATURATION LINE

fig. 7



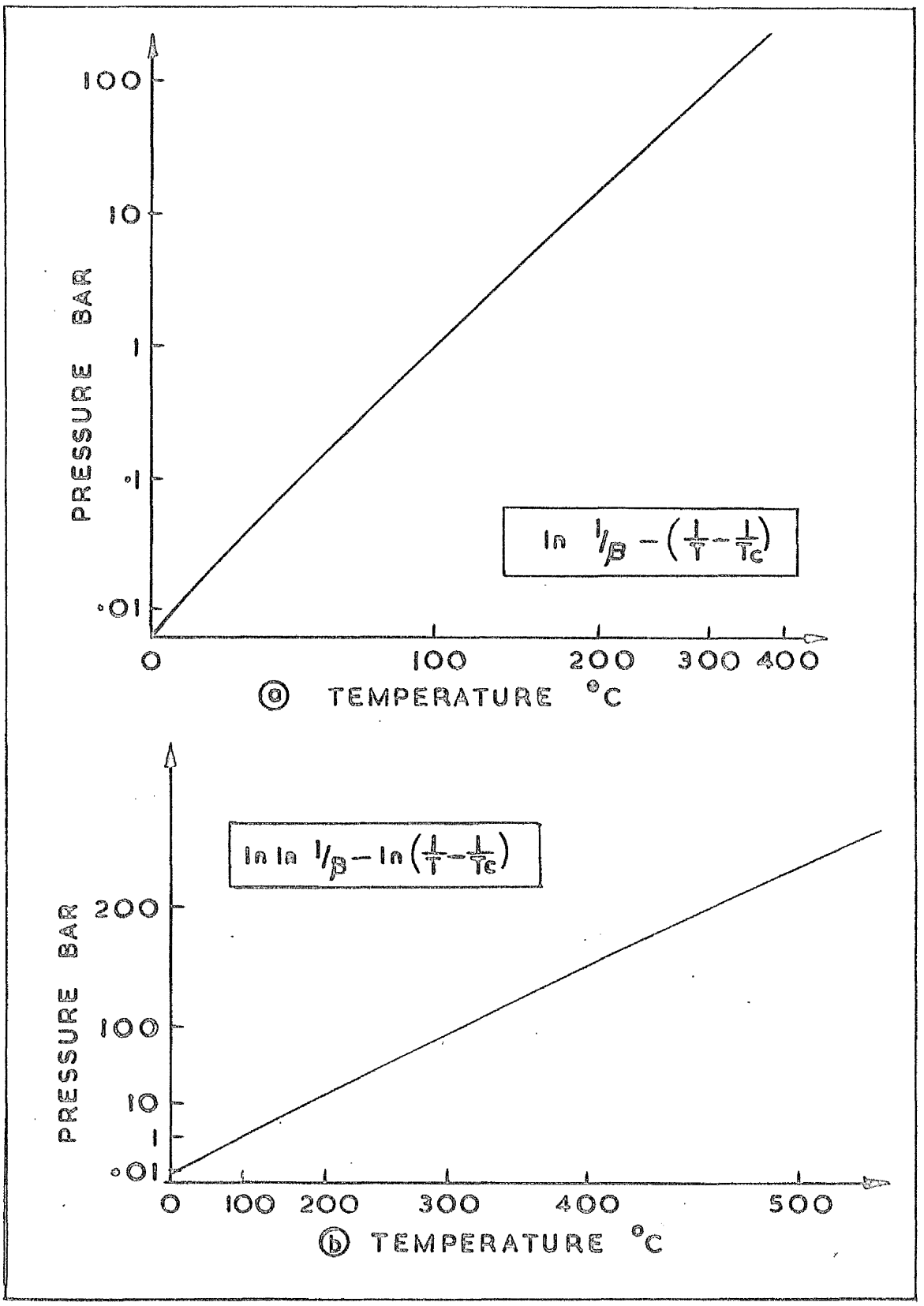
p AND t FOR THE SATURATION LINE

fig. 8



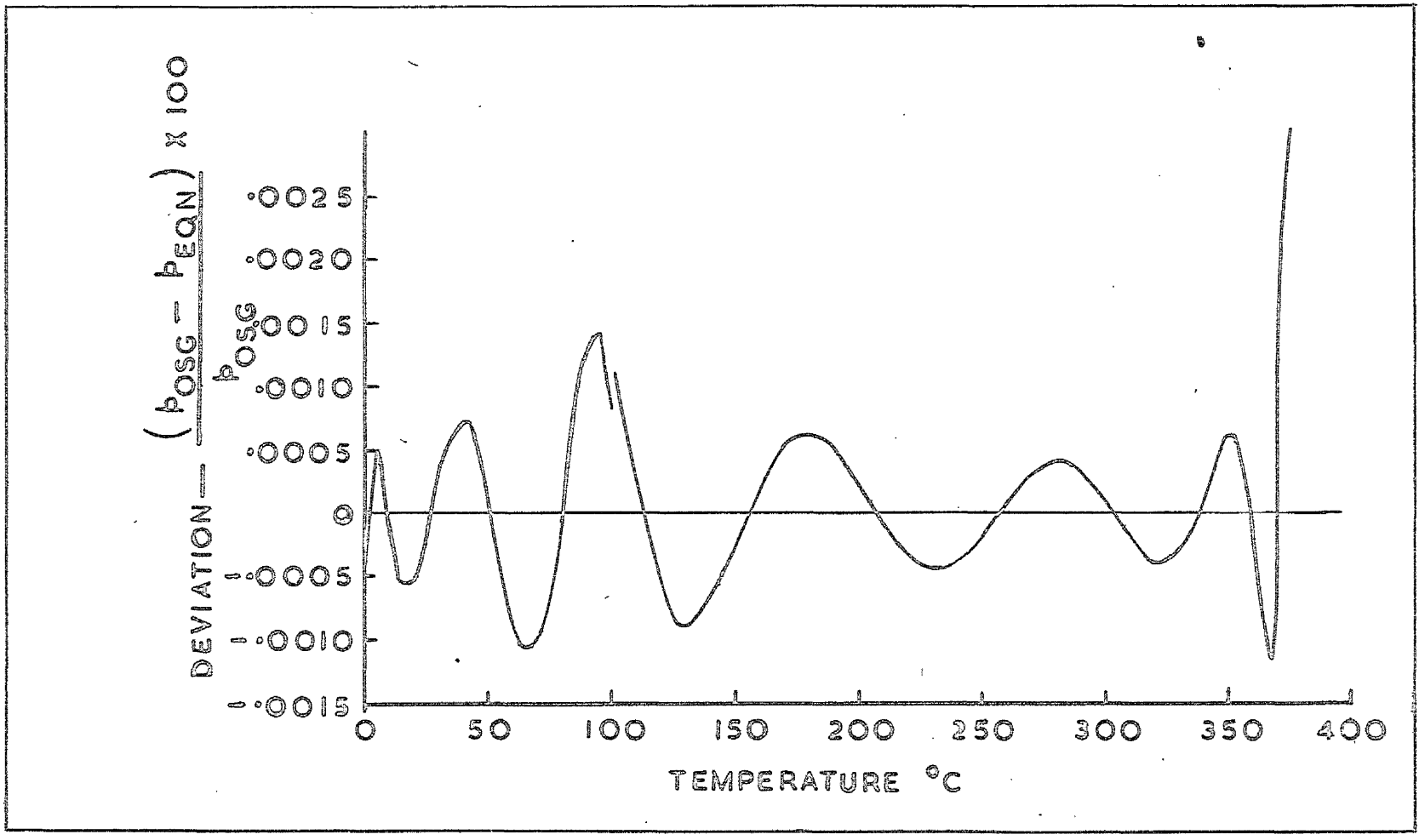
ln. p AND I/T FOR THE SATURATION LINE

fig. 9



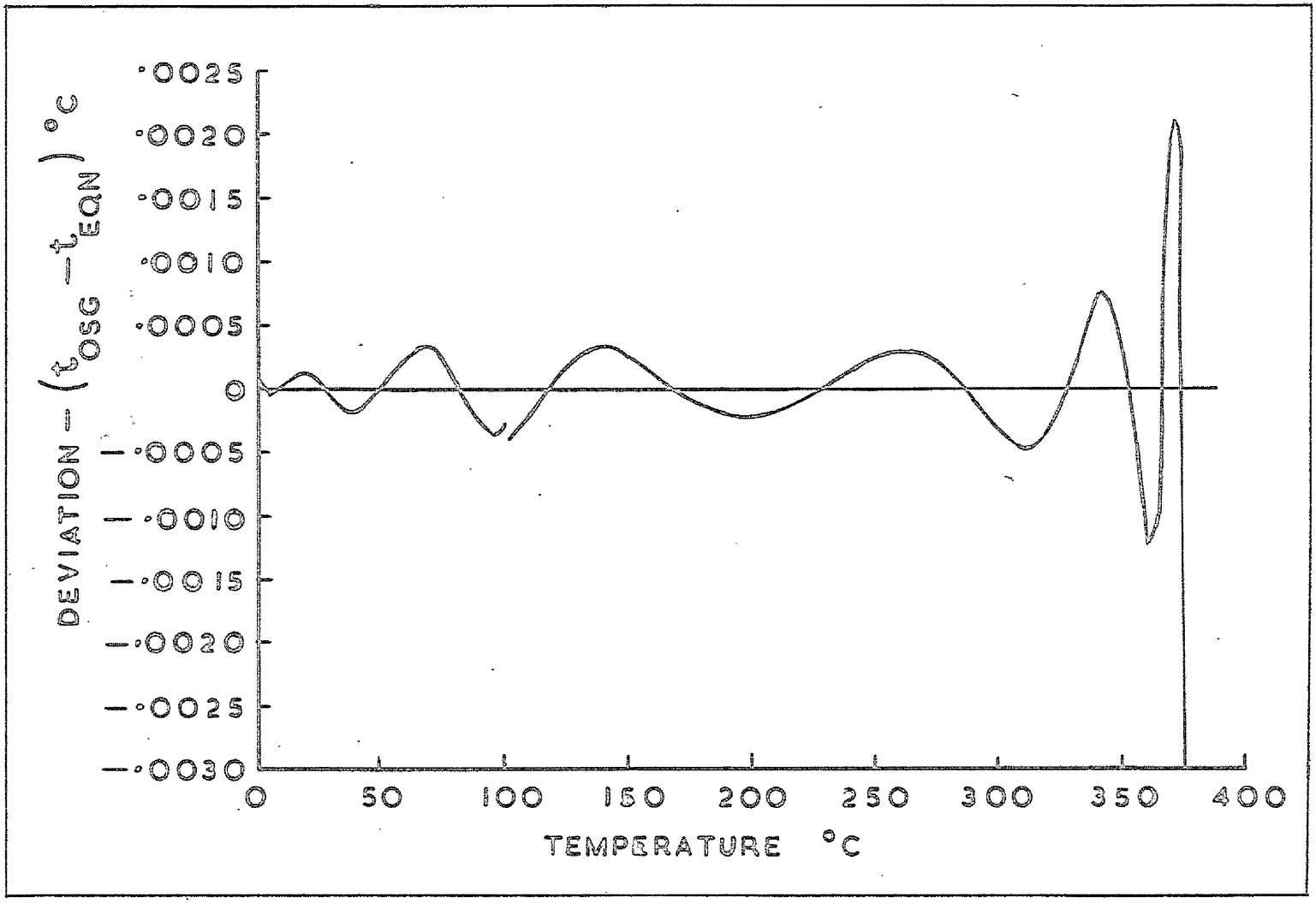
ln p AND (1/T−1/Tc) FOR THE SATURATION LINE

fig. 10



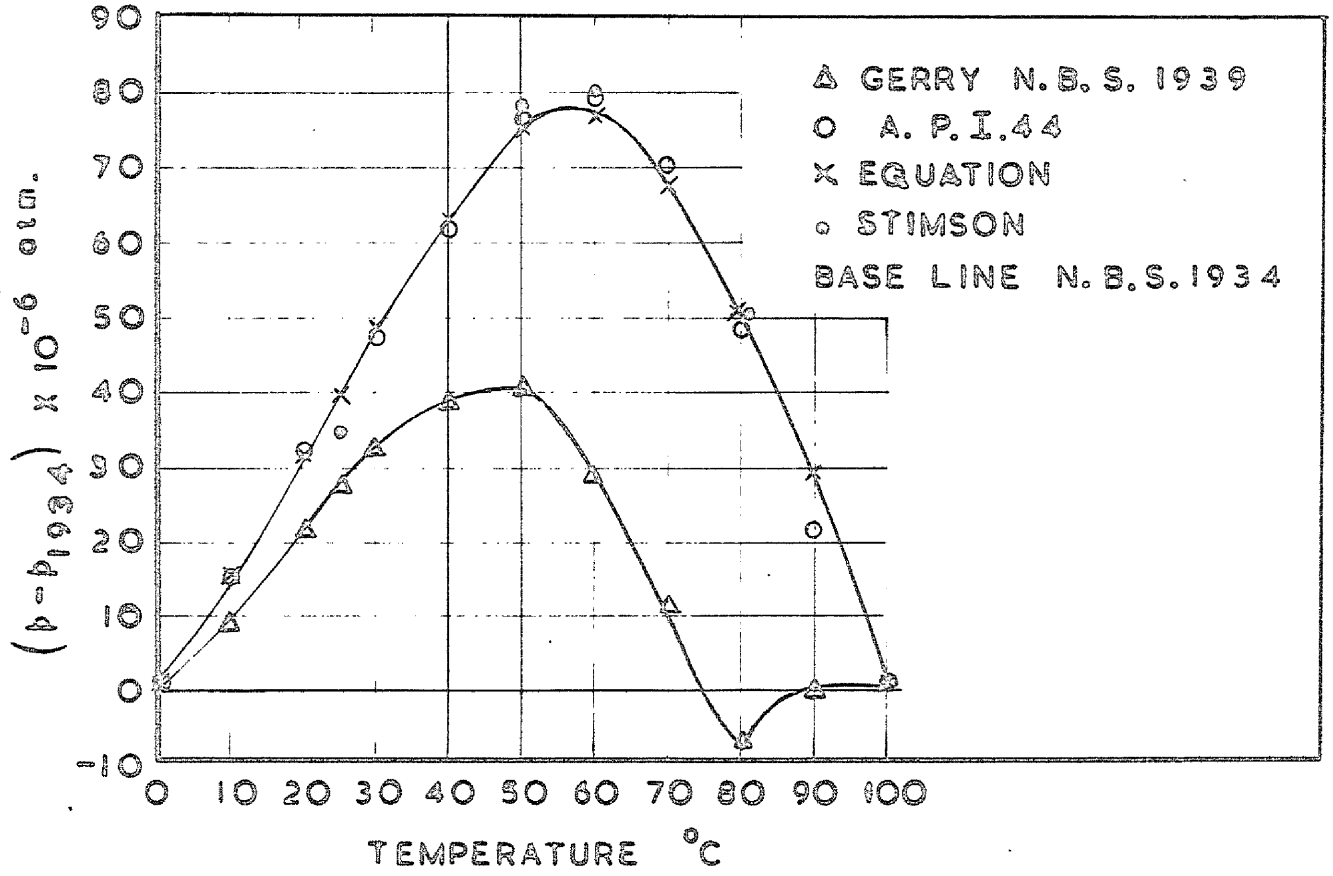
PERCENTAGE DEVIATION BETWEEN EQUATION (137) AND OSG VALUES

fig. 11



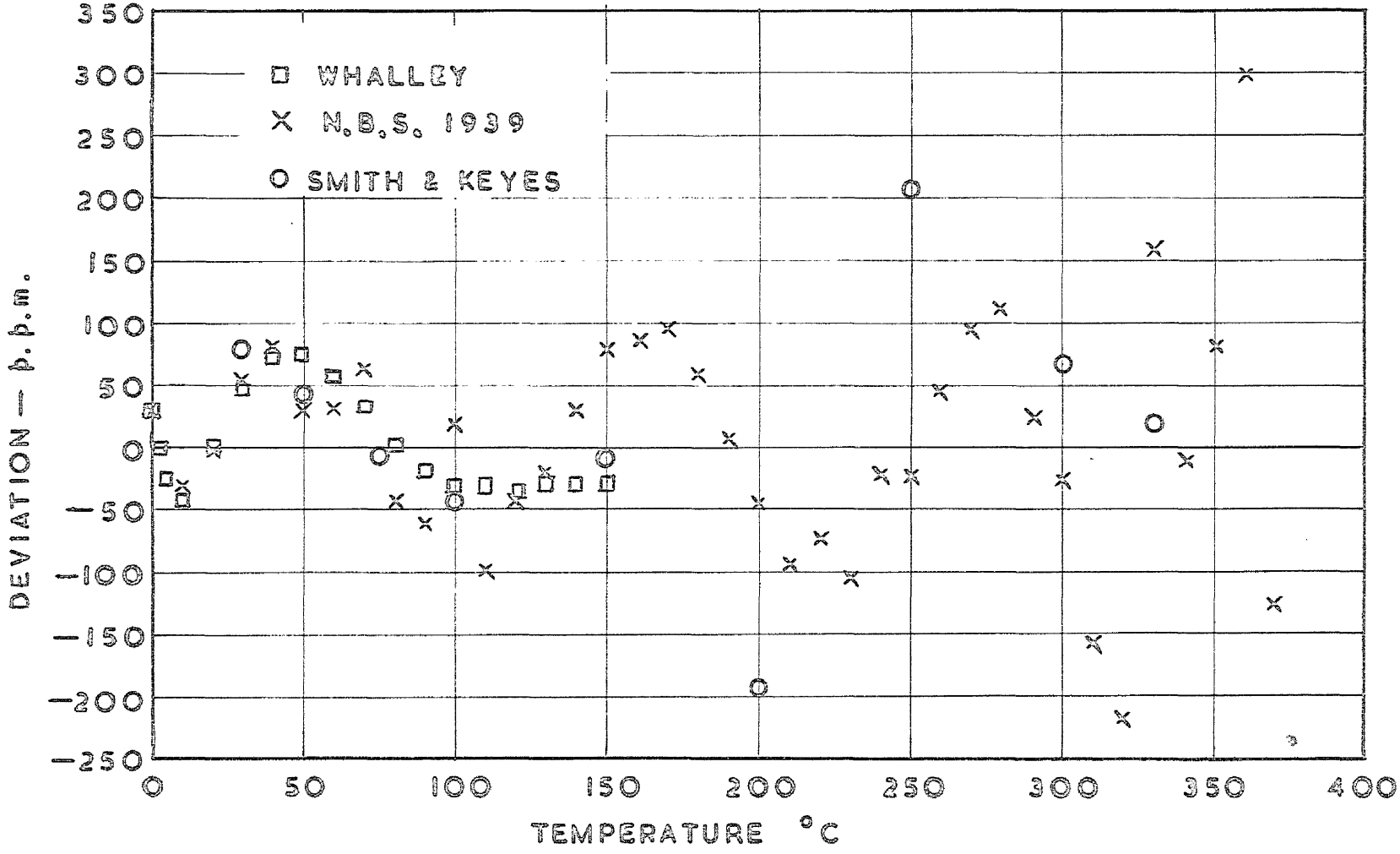
DEVIATION BETWEEN EQUATION (138) AND OSG VALUES

fig. 12



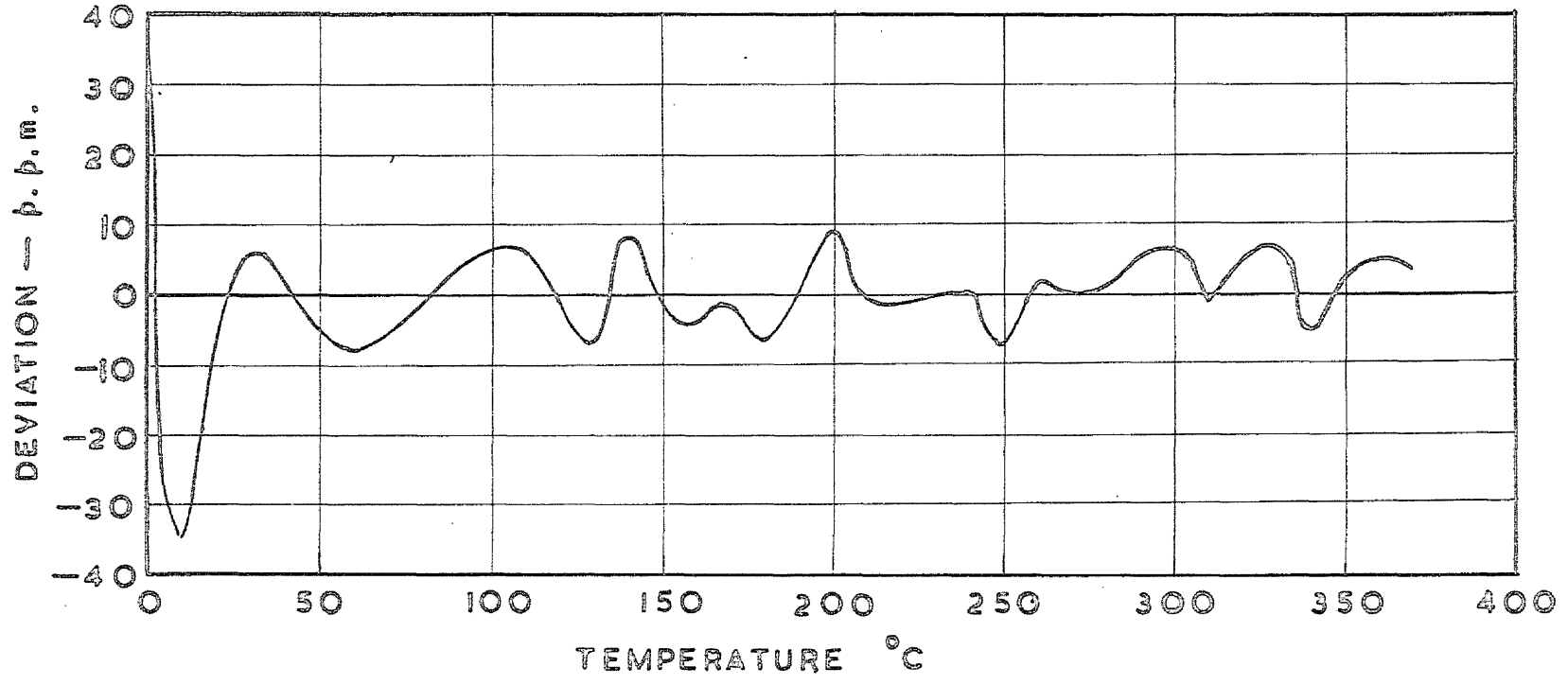
DEVIATIONS OF EQUATION (137 b), IST 1963 VALUES AND API 44 CORRELATION FROM 1934 NBS CORRELATION

fig. 13



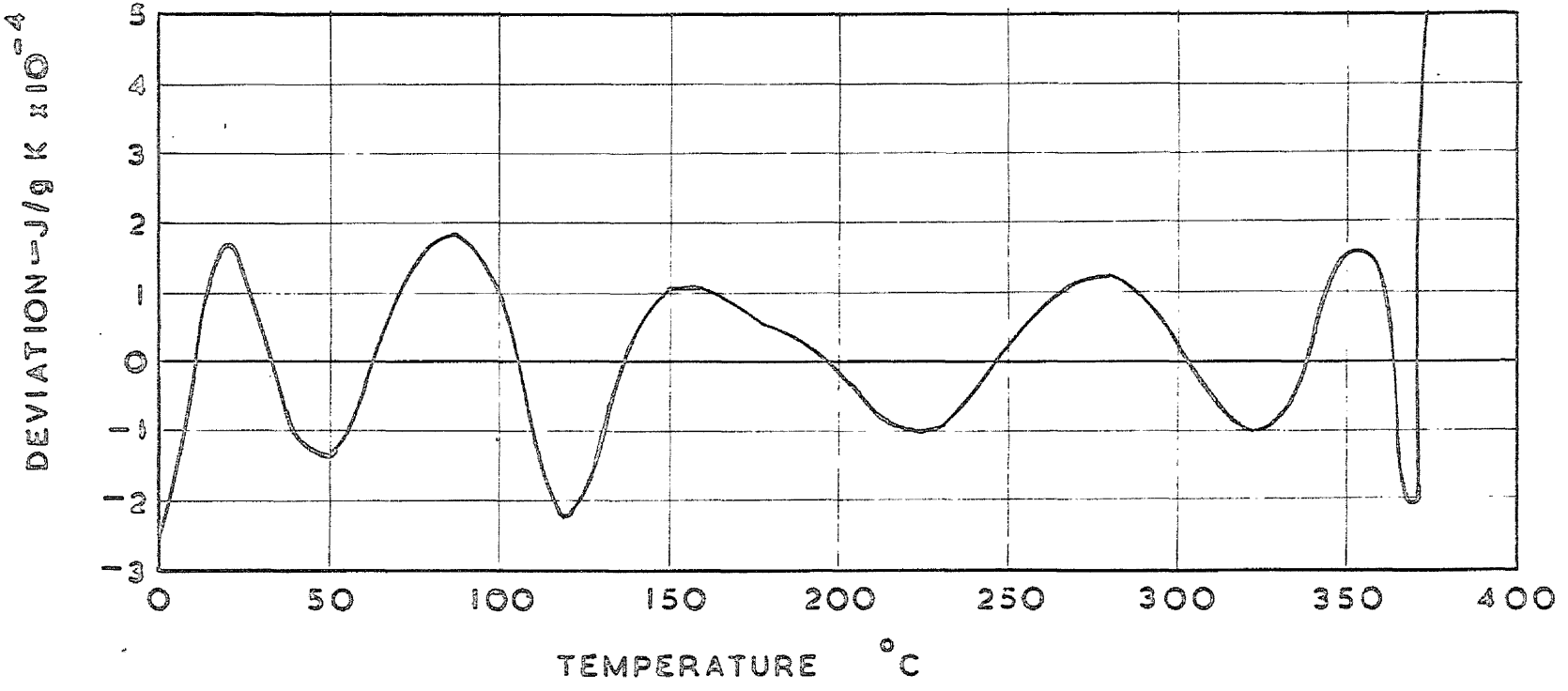
DEVIATION OF LIQUID VOLUME VALUES FROM EQUATION (139)

fig. 14



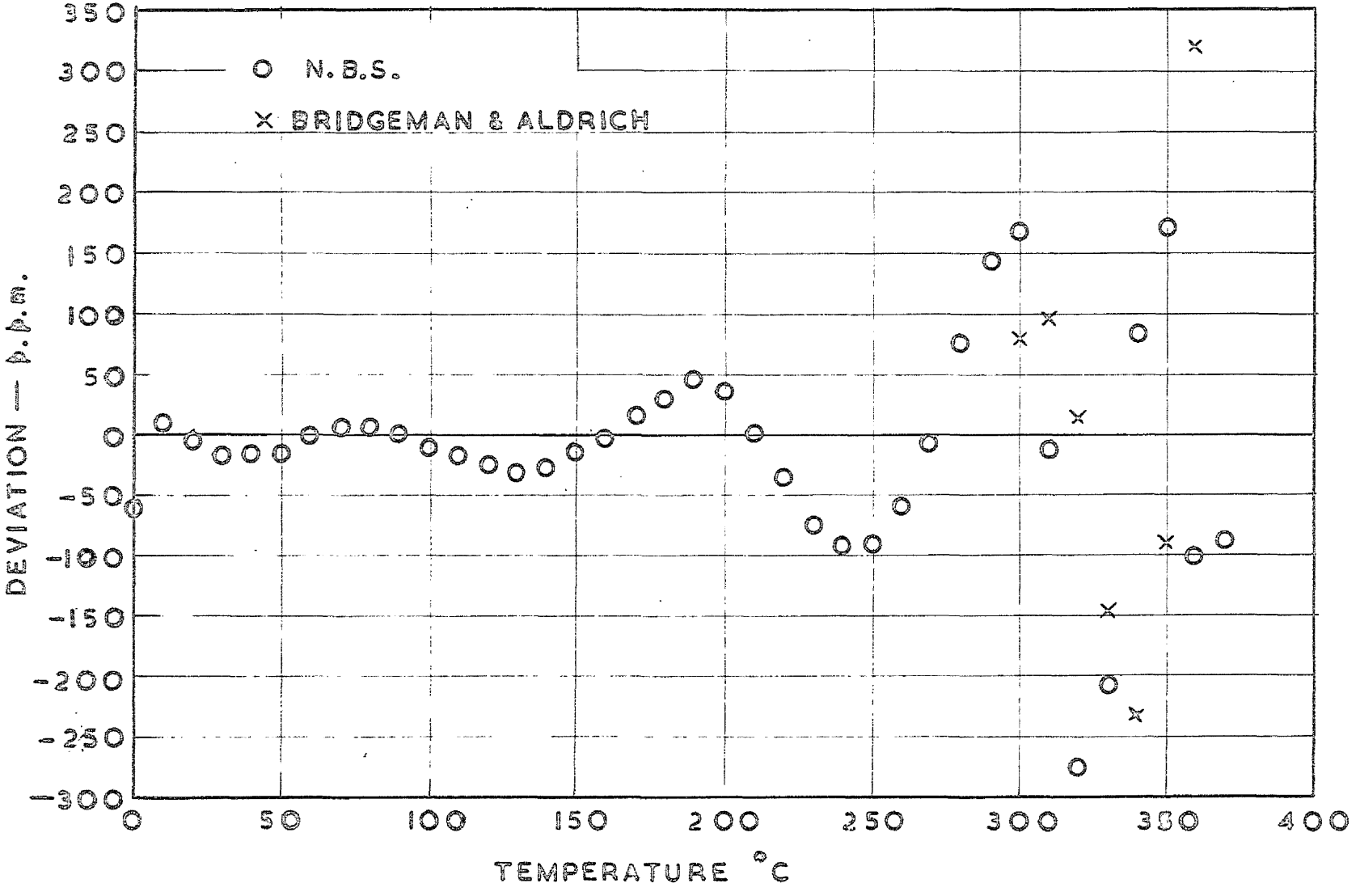
DEVIATION OF NBS FITTED λ VALUES FROM EQUATION (140)

fig. 15



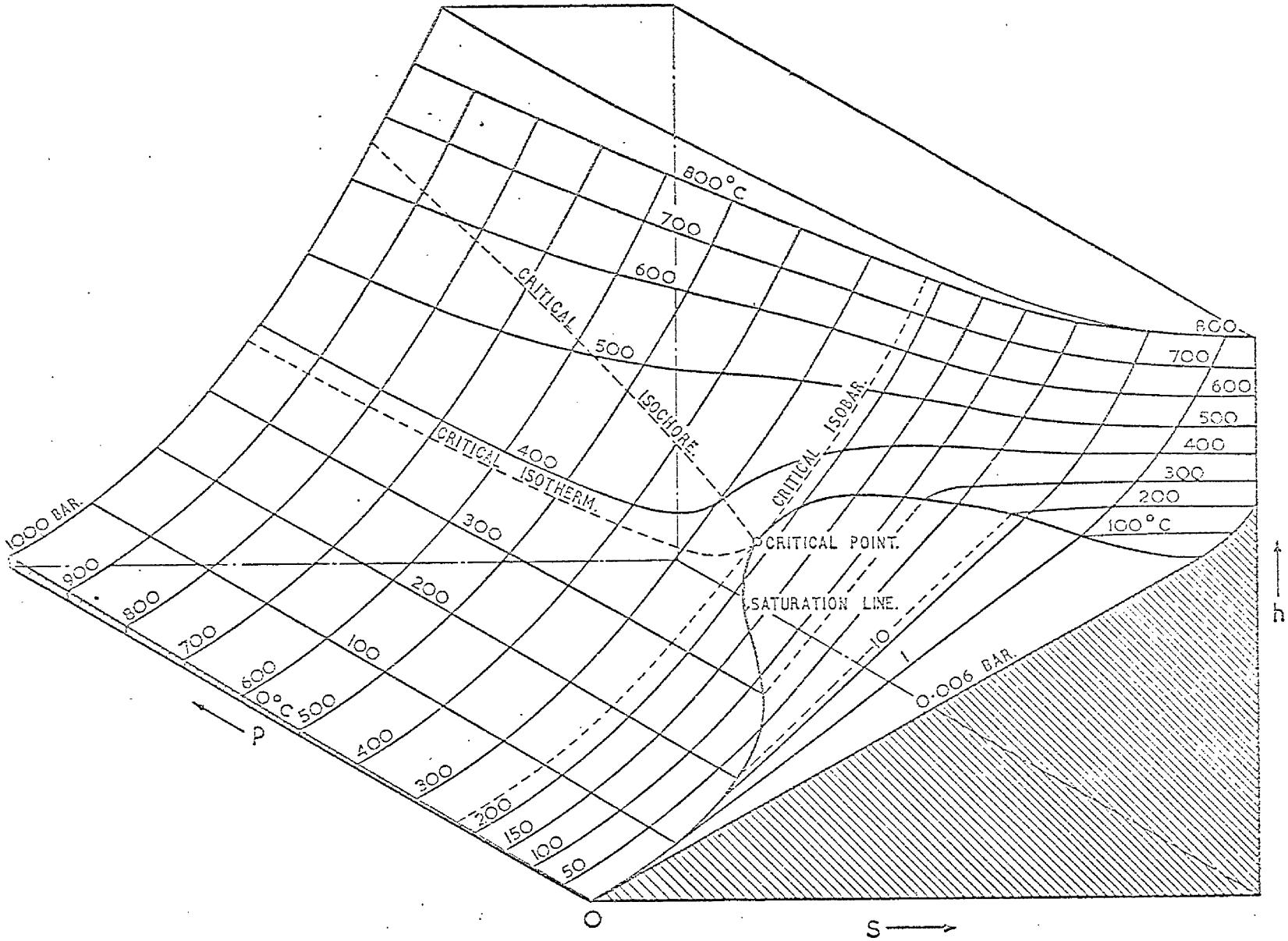
DEVIATION OF NBS FITTED $d\alpha/dT$ VALUES FROM EQUATION (140)

fig. 16



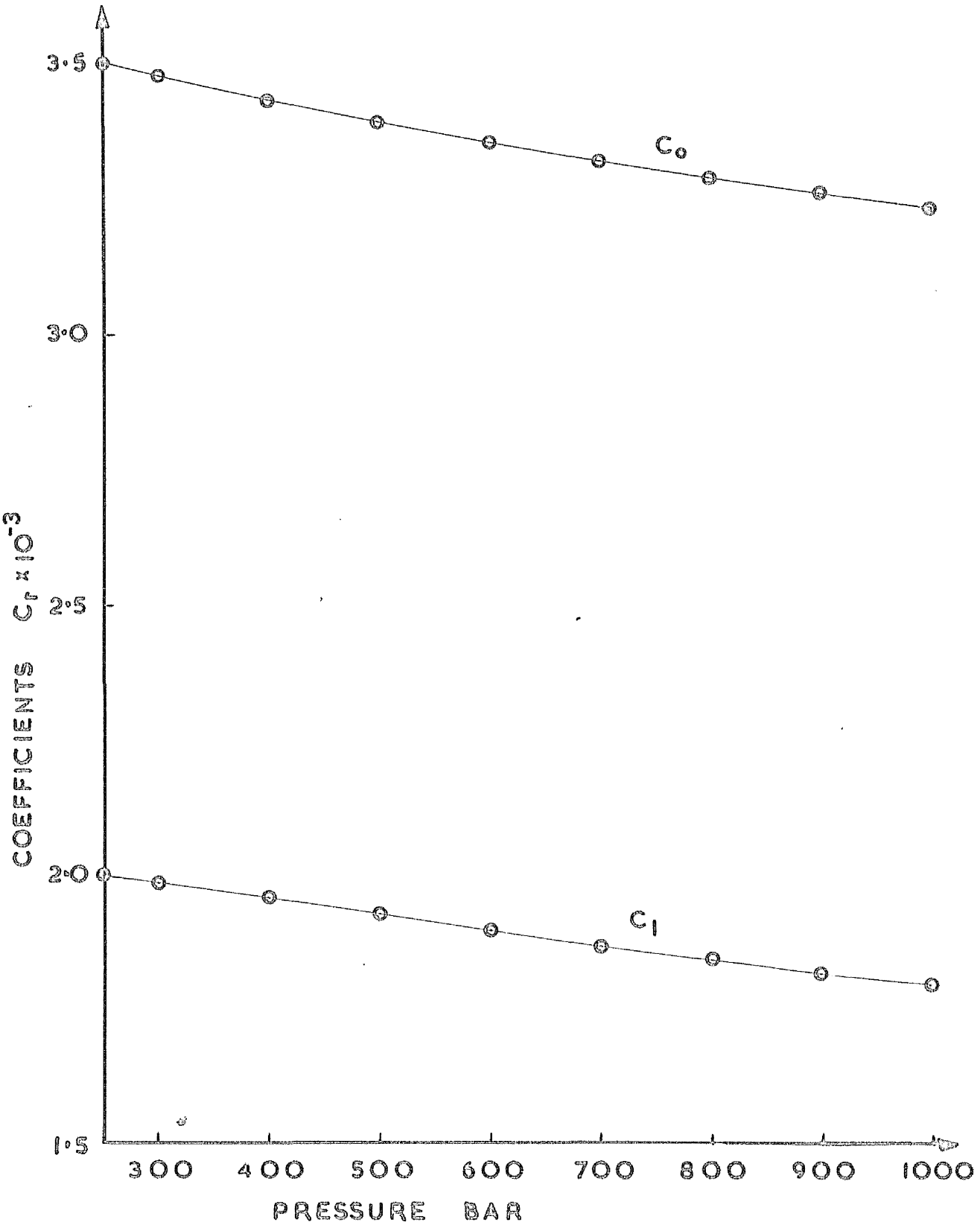
DEVIATION OF NBS γ OBSERVATIONS FROM COMPUTED VALUES

fig. 17



h-p-s surface of water substance.

fig.18



CHEBYSHEV COEFFICIENTS FOR EQUATION (151)

fig. 19

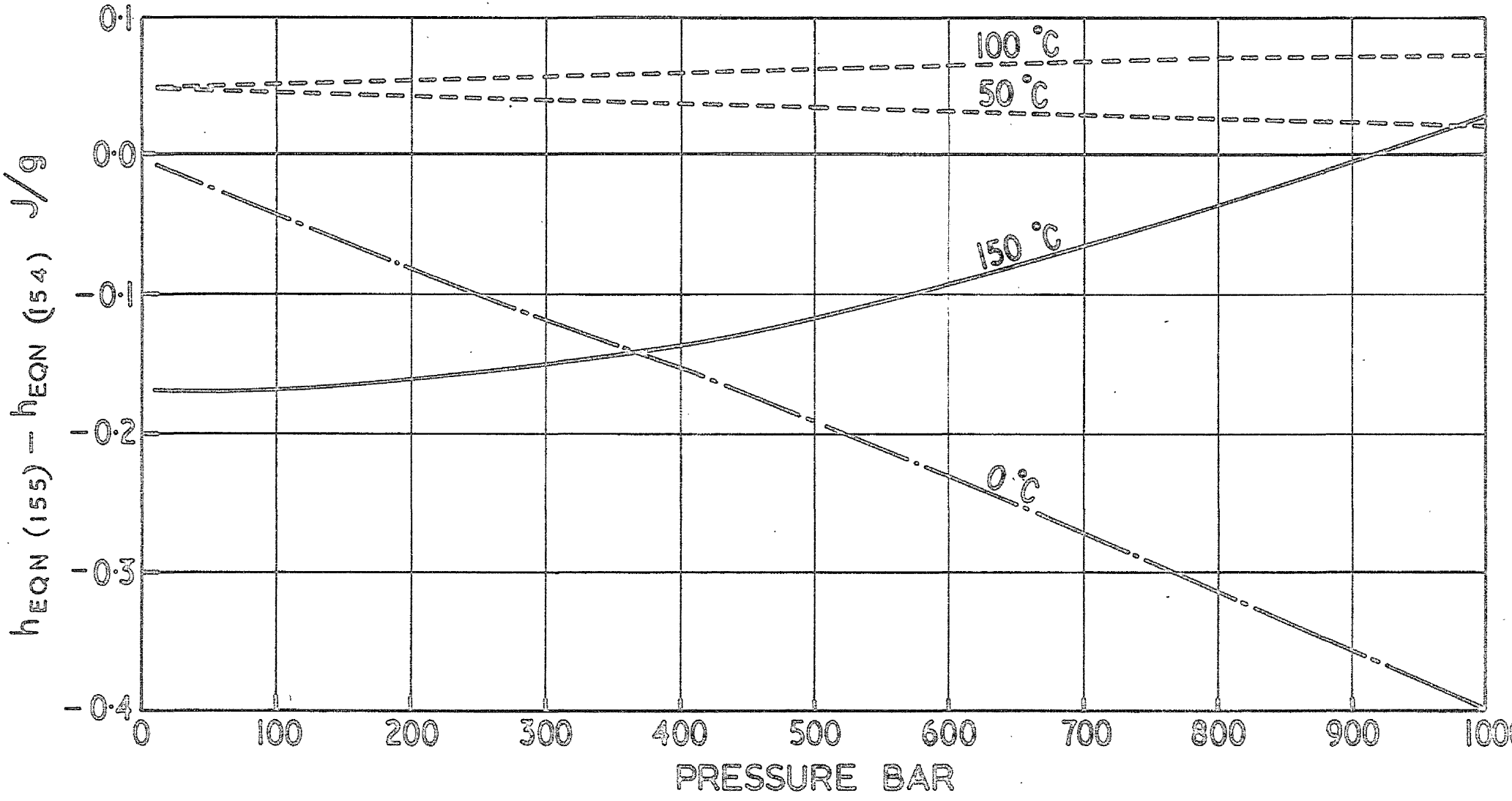


FIG. 20 ENTHALPY DEVIATION BETWEEN EQUATIONS (155) AND (154)

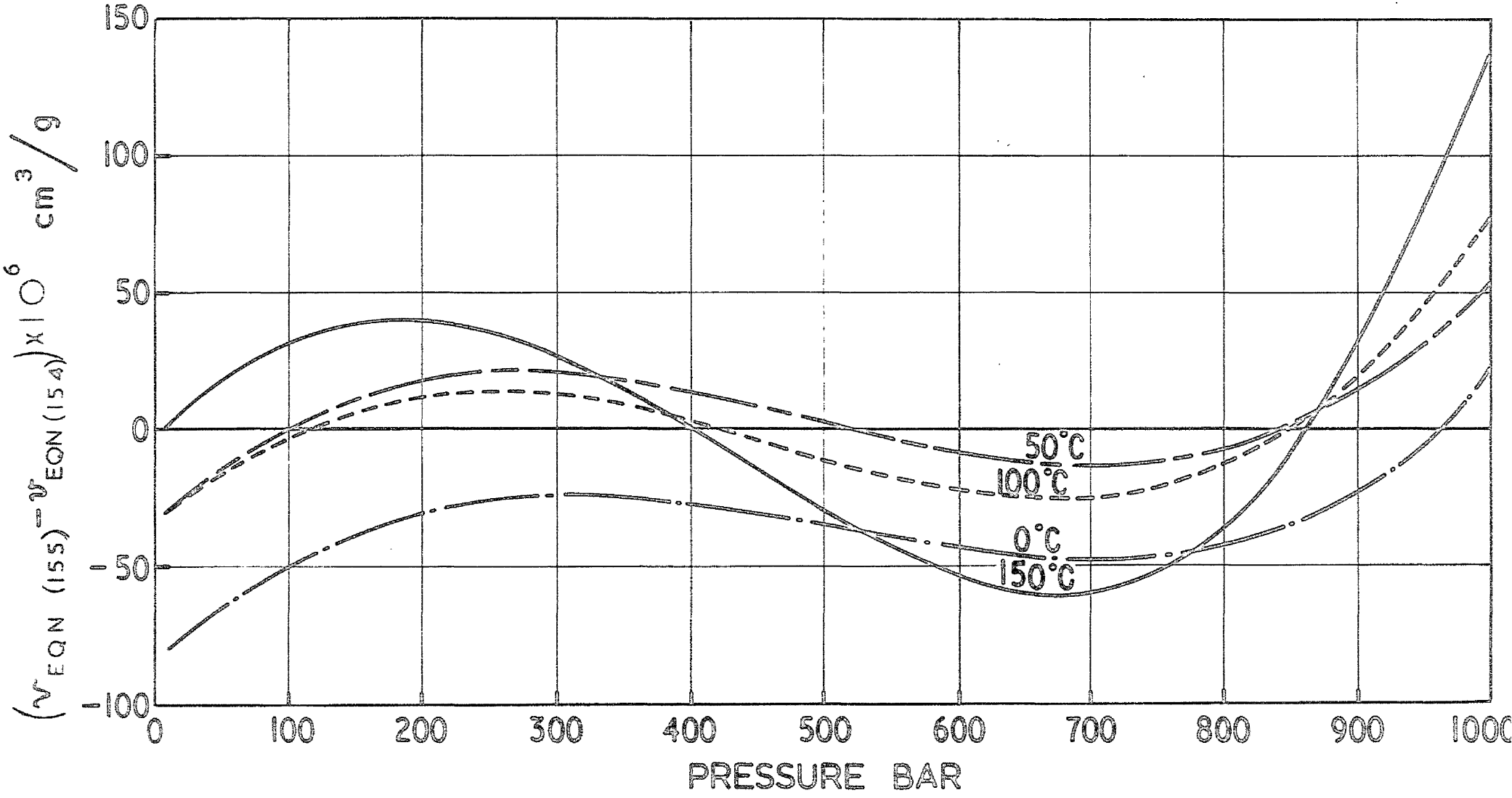
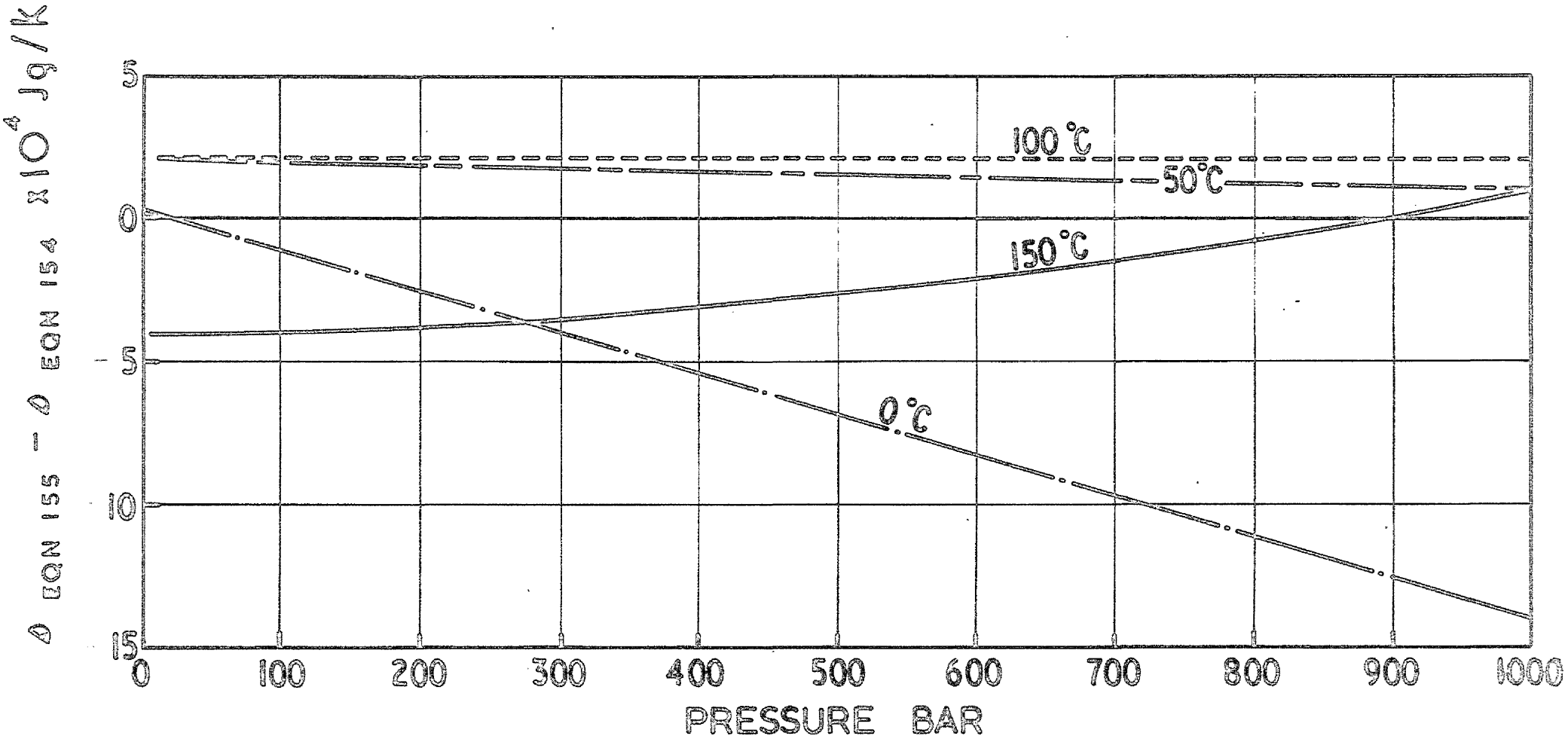
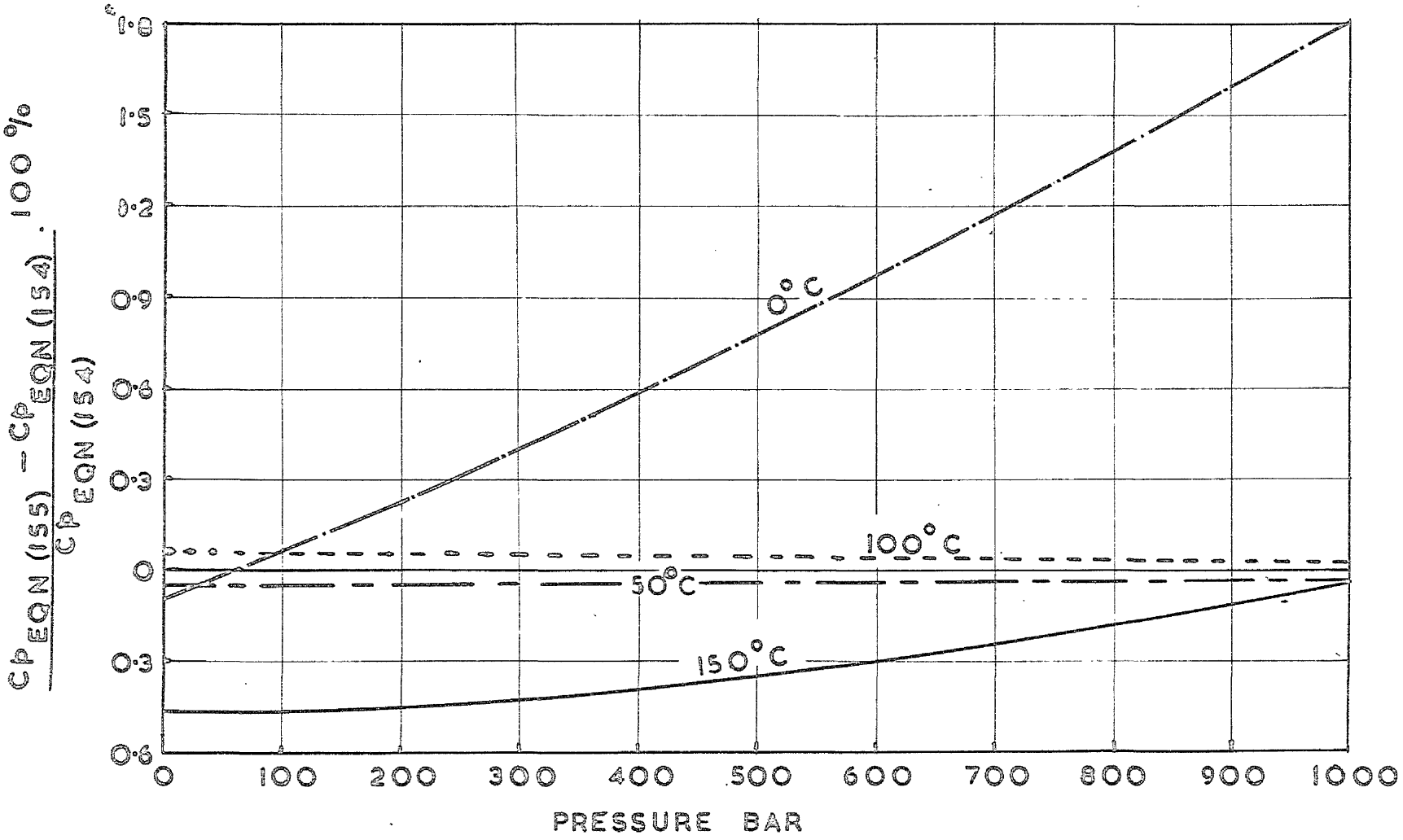


FIG. 21 VOLUME DEVIATION BETWEEN EQUATIONS (155) AND (154)



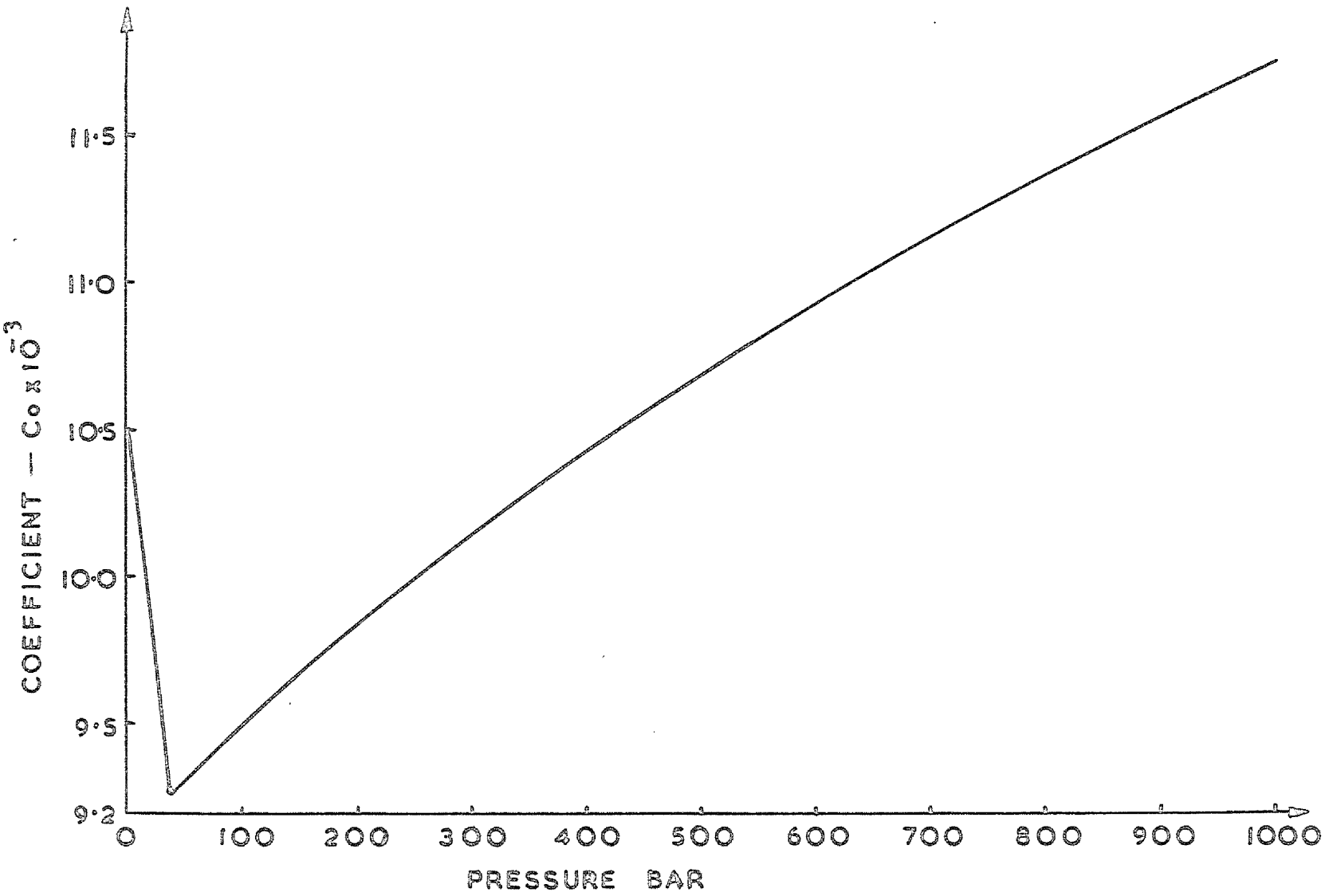
ENTROPY DEVIATIONS BETWEEN EQUATIONS (155) AND (154)

FIG. 22



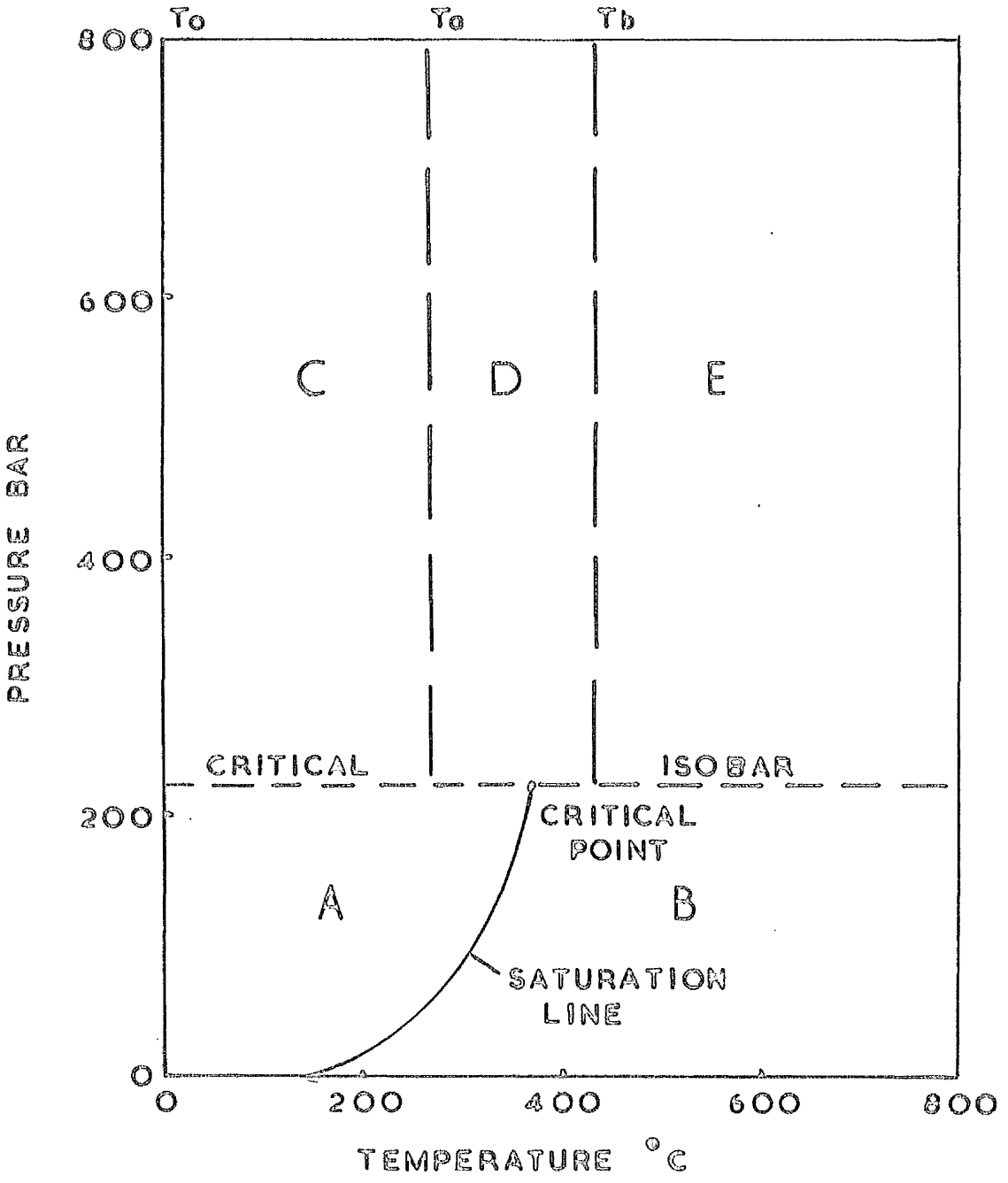
PERCENTAGE DEVIATION FOR C_p BETWEEN EQUATIONS (155) AND (154)

fig. 23



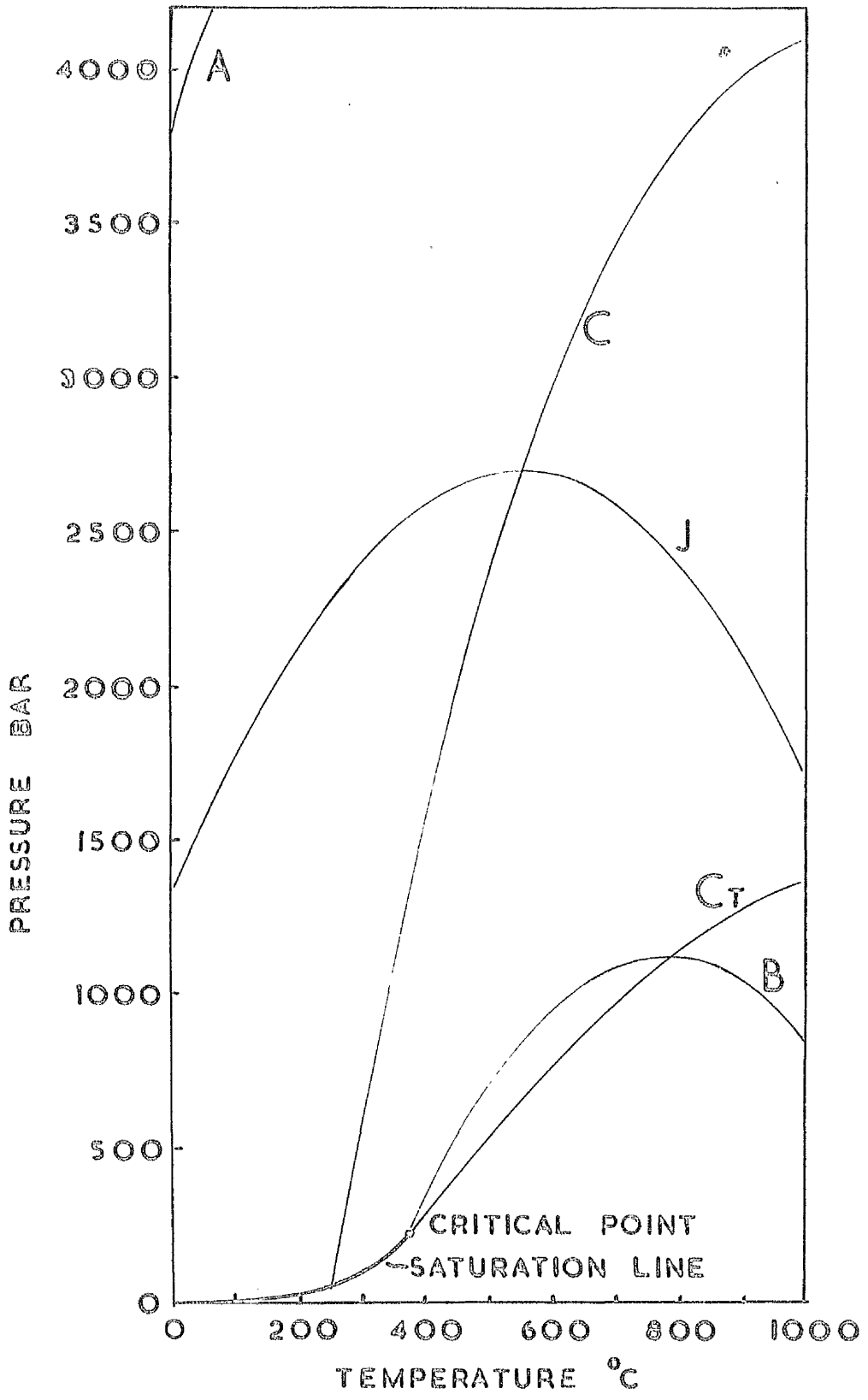
FIRST COEFFICIENTS FROM EQUATIONS (151) FOR JUZA'S DATA

fig. 24



SUGGESTED REGIONS FOR FUTURE SURFACE FITTING

fig 25



CHARACTERISTIC CURVES FROM JUZA

fig. 26